Investigation of Luminescent Diode Arrays
for Photochromic Film Recording.

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SECTION 1

Introduction and Summary

The work of this report is directed toward the optical recording of time-sequential information from a spatial array of hydrophones or other sensors. The time sequence of signals from the sensor array is initially a space-time matrix of data. An optical recording process is required which will convert this data into a two-dimensional spatial matrix.

Such a recording process will require the following elements:

1. A photographic recording film or other medium

2. A writing head capable of simultaneous recording of data in parallel columns on the film from many information channel

3. A hydrophone signal distributor to transfer the signal from each hydrophone to the matching channel of the writing head, with signal amplification or other input matching to assure compatibility with the writing head.

This report will assess the practicability of such a recording system in which the recording medium is photochromic film and the writing head is an array of luminescent semiconductor diodes. The diode arrays considered here will be made by neutron transmutation doping since this technique promises high density packing of luminescent diodes with high optical power density per unit area. The recording medium to be considered will be photochromic film because it can be repeatedly re-used, and therefore offers the possibility of long term use with a relatively low volume of film. It also offers the property of high resolution storage of the information.

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The important characteristic of photochromic film is its ability to change its optical density in a reversible manner, upon the absorption of optical radiation of specified wavelengths. The thermal fading rate is slow (minutes to hours) and the spatial resolution can be high - theoretically in the 100 angstrom range.

The optical density of a photochromic film will vary as a function of the wavelength - usually expressed in millimicrons $(m\mu)$ - of the incident radiation, and of the energy deposited (expressed in joules per cm^2 or millijoules per cm^2) as a function of wavelength. A photochromic film will usually have at least two wavelength ranges with opposite behavior: An activation wavelength range, within which the absorption of energy will increase the optical density of an initially transparent film; and a bleaching wavelength range, within whic the absorption of energy will decrease the optical density of the film. There will also be a neutral wavelength which will not affect the film and which can therefore be used for optical reading.

Luminescent diode writing heads have a number of potent al advantages for recording on photochromic film: The luminescent P-N junction area can be in close contact with the film leading to efficient utilization of the radiant energy. The radiant power density produced by electrical pulses can be appreciable, of the order of millijoules per cm^2 for short pulse lengths. The size of the illuminated region can be a few square mils, small enough to achieve a relatively high packing density of information on the film without requiring optics.

Another important consideration is the possibility of fabricating luminescent diodes in array configuration. Since many recording channels are required along the width of the film, a linear array of diodes is needed. Neutron transmutation doping was selected as a promising method for fabricating a luminescent diode array with relatively close spacing in a single step. This doping method, which is described in detail in Section 5, has the

capability of fabricating a linear array of P-N junctions of
almost arbitrary length, in a single semiconductor crystal, with
a diode-to-diode minimum spacing in the 10 to 30 mil range.

Summary of the Work

In Section 2 of this report the properties of photochromic
films are described and the characteristics of luminescent diode
writing heads are briefly reviewed. The specifications for a
multiple-channel photochromic recording system are given. A
detailed discussion is given of the system aspects of photo-
chromic film recording which will emphasize the critical
parameters in assessing such a system.

The important characteristics of photochromic material are
1) its reversibility, 2) its spectral range, 3) the energy
density required for bleaching and 4) its expected lifetime
in cycles of use. A program of measurements was carried out on
a number of available photochromic materials to determine these
characteristics. The measurements and results are described in
Section 3.

Photochromic material measurements are described in Section
3.1. The results are summarized in Section 3.2. It was found
that only one available material had the spectral range and low
energy density for bleaching that is at all compatible with
luminescent diodes. This is the VL-316A film in glass laminate
form. It was also found that the lifetime in use cycles of the
system is relatively limited.

The lifetime of the photochromic film is limited by the
deterioration of the chemical compound in the ultraviolet
activation process. As the deterioration proceeds, more ultra-
violet light is required to produce a given density change.

Eventually the film is no longer sensitive to either activation or bleaching light. Measurements on the VL316A film (the most satisfactory) indicate an expected lifetime of 800 cycles.

Experimental attempts were made to increase film lifetime by conducting activations in several chemically different atmospheres. No significant differences were observed. This is discussed in Section 3.3.

It is pointed out in Section 3 that the bleaching mode in photochromic films requires radiation in the 5000 to 7000 angstrom range. It is also necessary to achieve an energy density of the order of 10 to 20 millijoules per cm^2 to obtain bleaching. In Section 4 we consider the attainability of this wavelength and energy density with semiconductor luminescent diode arrays which can be fabricated by transmutation.

Gallium arsenide phosphide can be produced to emit at any wavelength in the range from about 5900 $\AA$ to 9100 $\AA$ depending on its composition. The required wavelength can be obtained by properly specifying the value x in GaP_xAs_{1-x}. The greater the value of x, the lower is the wavelength emitted.

Any semiconductor composition in the family GaP_xAs_{1-x} can be doped in a junction array configuration by neutron transmutation techniques. At the beginning of this investigation it was intended to select a composition that is compatible in frequency with a satisfactory photochromic material. When it was found that no photochromic material had a sufficiently long life cycle to satisfy the system requirements, it was decided to conduct the power compatibility measurements with the most convenient and most easily obtainable semiconductor material in this family, gallium arsenide. Results obtained for GaAs would in addition be directly applicable for development of a diode array for multichannel recording on conventional photographic films.

Measurements were made on gallium arsenide luminescent diodes produced by 1) neutron transmutation and 2) by diffusion. In both cases power densities of 50 to 100 milliwatts per cm^2 were measured under CW conditions. With good heat sinking and pulsed power this should permit sub-millisecond writing speeds on the best photochromic film.

The application of neutron transmutation techniques to diode array fabrication in the gallium arsenide phosphide family of compounds is described in Section 5.

Neutron transmutation techniques can make a significant contribution in the development of multi-channel recording on photochromic film (and alternatively, on photographic films) by means of the capability for fabricating a high linear density of diodes on a single wafer of semiconductor, each diode having a small emitting area. An array of 100 diodes over a 1-inch width of semiconductor wafer is an attainable objective. This corresponds to a 10-mil spacing between diodes, each diode having a radiation-emitting area of 5 to 10 square mils. In the present program the more modest objective of a 30-mil diode spacing was set. This goal was attained and a four diode array with 30-mil spacing was made. The radiation-emitting area of each diode was 15 square mils.

Transmutation techniques have thus been used in this work to make an integrated linear optical array fabricated on a single monolithic slice of gallium arsenide. This integrated device includes all electrical connection points and all infrared-emitting junctions. Furthermore, we have shown that despite the small size and compactness of the diode array, a sufficient intensity for film recording is available from each P-N junction element.

It had originally been planned to perform the neutron transmutation irradiations for production of the diode array writing heads in the Oak Ridge Reactor, with which we have extensive experience. Two capsules were planned, one capsule to produce individual diodes and some small arrays (five junctions or less) and one capsule to produce larger arrays. However, after the photochromic material studies were completed we were informed that increased usage of the Oak Ridge Reactor by Oak Ridge National Laboratory would make scheduling of experiments extremely uncertain. It was therefore decided to use another available reactor, the Air Force Nuclear Test Facility (AFNTF) at Wright Patterson Air Force Base.

The first capsule was prepared and irradiated. It was found however that the gallium arsenide specimens had all been over-irradiated. Not only had the originally P-type unshielded regions been converted to N-type, but the shielded P-type regions, which should have remained P-type were also converted to N-type.

Detailed analysis of the first capsule specimens showed the reason for this over-irradiation. The non-thermal (higher energy) part of the neutron flux spectrum is significantly higher in the AFNTF than in the ORR. This is particularly important for gallium arsenide which has neutron absorption resonances at the higher neutron energies which are present in the AFNTF. The significance of the lower cadmium ratio in the AFNTF is presented in detail in Section 6.1.

Once this point was realized, a second capsule was prepared to replace the first capsule. This irradiation was successful in producing single diodes and four-element arrays. This capsule is described in detail in Section 6.

The successful gallium arsenide irradiation capsule included several specimens which had been exposed with radiation dies to produce four-element arrays. One of these four-junction diode arrays was fabricated into a four-channel fil'. writing head, which was tested successfully on 35 mm infrared film. A simple four-channel recorder was built and demonstrated. The recorder was delivered to the U.S. Navy Underwater Sound Laboratory, New London, Connecticut. This four-channel diode array film recorder is described in Section 7 as typical of larger arrays which can be built.

SECTION 2
Photochromic Film Recording for Optical Correlators

The work of this report is directed toward the optical processing of time-sequential information from an array of hydrophone heads. Each hydrophone head presents an electrical signal continuous in time; the hydrophone array may consist of hundreds of such heads. It is desired to record all signals from the array sequentially in time on an optical recording medium, e.g., a photochromic film. The time sequence of signals from the hydrophone array is initially a space-time matrix of data. The optical recording process converts it into a two-dimensional spatial matrix, for example with the x-coordinate characterizing the hydrophone array element and the y-coordinate (proportional to the film movement speed) characterizing the time point of the data.

When the data is in this spatial matrix form it is ready for optical processing. The data at each point can be considered an opaque spot in an otherwise transparent medium. In analog recording the optical density (to be defined below) of the spot will be proportional to the hydrophone element signal intensity represented by that spot at that point in time. In digital recording, the spot will be either completely opaque or transparent and a series of such spots will constitute the binary representation of the signal from the hydrophone at a point in time. An analog-to-digital converter will be necessary to digitalize the hydrophone signal.

The spatial matrix of data produced in this way is suitable for optical correlation processing, e.g. its spatial frequency spectrum can be obtained or its autocorrelation function or its cross-correlation function with various reference patterns. These calculations are necessary for the detection, recognition, and classification processes in using the hydrophone array. What

should be emphasized is that optical correlation processing is an extremely efficient means for performing these calculations. For a two-dimensional matrix one can show that optical processing is far more effective than digital computer processing, to the point where many extremely significant recognition and classification processes which cannot be attempted by digital computer analysis are directly amenable to optical correlation processing. When results are needed in real time or in almost-real time, optical processing is also of unique significance.

The operation of such an optical processor depends on a suitable optical recording process, which will prepare the two-dimensional spatial matrix of data which is required. The recording process will require the following elements:

1. A photographic recording film or other medium

2. A writing head capable of simultaneous recording of data in parallel columns on the film from many information channels

3. A hydrophone signal distributor to transfer the signal from each hydrophone to the matching channel of the writing head, with signal amplification or other input matching to assure compatibility with the writing head

This report will assess the practicability of such a recording system in which the recording medium is photochromic film and the writing head is an array of luminescent semiconductor diodes. The diode arrays considered here will be made by neutron transmutation doping since this technique promises high density packing of luminescent diodes with high optical power density per unit area. The recording medium to be considered will be photochromic film because it can be repeatedly re-used, and therefore offers the possibility of long term use with a relatively low volume of film. It also offers the property of high resolution storage of the information.

2.1   Properties of Photochromic Film as a Recording Medium

A photochromic material is characterized by having two states with different absorption spectra, in which absorption at certain frequencies causes the material to change from one state to the other:

State A (Activation)
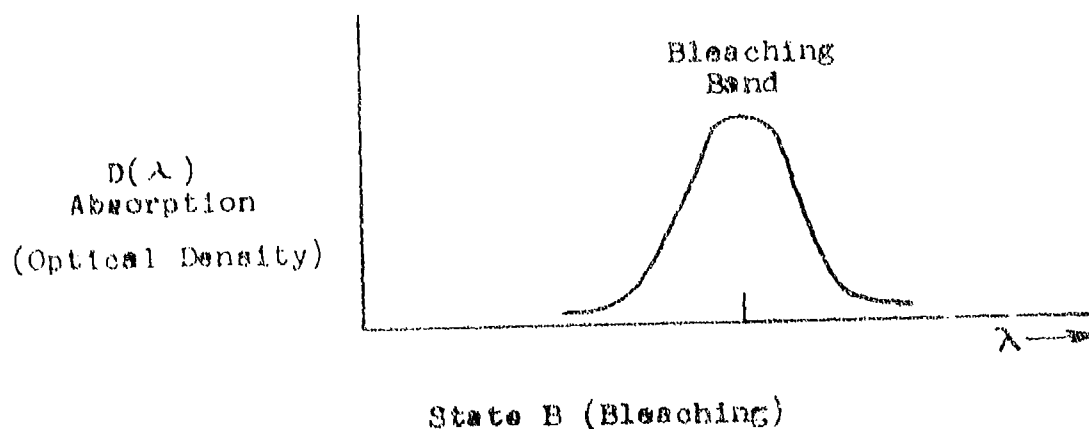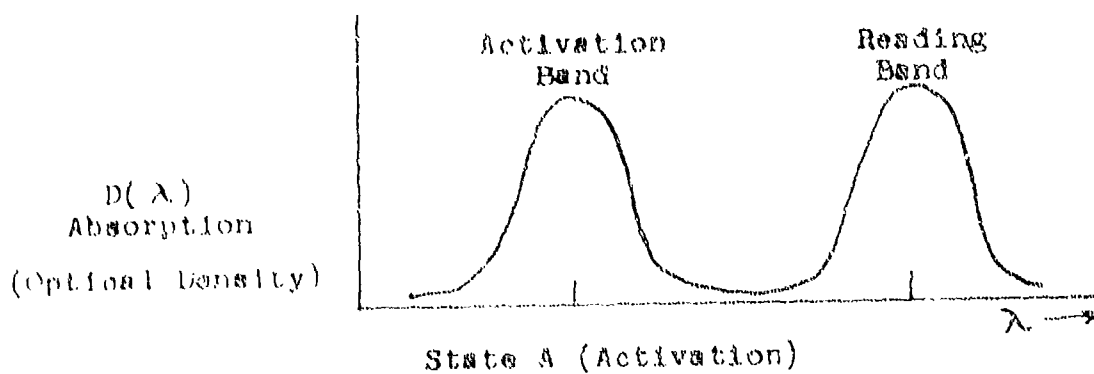
State B (Bleaching)

Figure 1.   Schematic Characteristic for
a Photochromic Material

State A has two absorption bands, as shown, one of which is
called the activation band and the other the reading band. State
B has one absorption band, falling in wavelength between the
activation band and the reading band of state A. This is called
the bleaching band. When in state A, if light in the activation
band is absorbed, the material switches to state B. When in state
B, if light in the bleaching band is absorbed, the material
switches to state A. In state A if light in the reading band is
absorbed, the state does not change. Hence this band can be used
for sensing the state without changing it.

It is apparent therefore that change of state can take place
either by activation or by bleaching; either of these bands can
be used for recording the infromation, while the sensing or reading
takes place using light in the reading band.

The writing can take place in one of two ways. (1) Initially
the material is in state A. Activation is used to convert it to
state B, and the absence of the reading band indicates that the
film has been written upon. (2) Initially the material is in
state B. Bleaching is used to convert it to state A, and the
presence of the reading band indicates that the film has been
written upon.

The important properties of photochromic film as an optical
recording medium may be summarized under the following headings:

1. write-read-erase modes
2. spectral transmittance and spectral absorpton
3. sensitivity of optical density changes to en rgy input
4. reversibility
5. spatial resolution
6. thermal fading rate

These properties will now be briefly described.

The important characteristic of photochromic film is its ability to change its optical density in a reversible manner, upon the absorption of optical radiation of specified wavelengths. The thermal fading rate is slow (minutes to hours) and the spatial resolution can be high - theoretically in the 100 angstrom range.

The optical density of a film (typical films of transparent plastic are of the order of 3 mils thick) is defined as

$$\text{optical density} = D = \log \frac{I_1}{I_2} = \log \frac{1}{T}$$

where I_1 is the incident radiant flux and I_2 is the transmitted radiant flux. T is the transmittivity of the film. The film will be considered a transparent medium in which one loads photochromic compounds (either in the bulk or on the surface) in various concentrations. We shall measure radiant flux in watts or milliwatts per cm^2.

Very often the optical density D is expressed in decibels:

$$D \text{ (in db)} = 10 \log \frac{I_1}{I_2} = 10 \log \frac{1}{T}$$

The optical density of a photochromic film will vary as a function of the wavelength - usually expressed in millimicrons or $m\mu$ - of the incident radiation, and of the energy deposited (expressed in joules per cm^2 or millijoules per cm^2) as a function of wavelength. A photochromic film will usually have at least two wavelength ranges with opposite behavior: An <u>activation</u> wavelength range, within which the absorption of energy will increase the optical density of an initially transparent film; and a <u>bleaching</u> wavelength range, within which the absorption of energy will decrease the optical density of the film. Usually there will also be a <u>neutral</u> wavelength

range between the activation range and the bleaching range, in which there will be no effect on the optical density. The activation range will usually be in the ultraviolet or deep violet-blue, while the bleaching range will usually be in the green-yellow, orange-red, or infrared. For a typical photochromic glass, Megla* gives the following ranges:

Activation: Between 330 mμ and 400 mμ
Neutral: Between 430 mμ and 530 mμ
Bleaching: Between 530 mμ and 630 mμ

The existence of these three wavelength ranges, whose optical effects are widely different from one another, are the basis for optical recording on photochromic film. The activation wavelength range and the bleaching wavelength range have opposite effects. The neutral wavelength range permits a probing beam or probing function which can read the recorded data without writing or erasing. There are two systems of recording with photochromic film:

System 1

Write: Uses the bleaching mode
Read: Uses the neutral wavelength or probing function
Erase: Uses the activation mode

System 2

Write: Uses the activation mode
Read: Uses the neutral wavelength or probing function
Erase: Uses the bleaching mode

Since solid state writing heads with high bit resolution can be made in the bleaching wavelengths but not (to date) in the ultraviolet activation mode, only System 1 will be useful for optical computer applications.

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* Megla, G.K., "Optical Properties and Applications of Photochromic Glass", Applied Optics, June 1966, p 945

Spectral Transmittance and Spectral Absorption

The spectral transmittance is given by a functional relation between optical density D and wavelength λ , of the form

$$D = D(\lambda)$$

This is called the activation spectrum in the activation range, and the absorption spectrum in the bleaching range. It can be measured using a scanning monochromator in conjunction with a xenon arc lamp. The optical density can be measured with a densitometer. Tne saturation optical density will depend on the film thickness.

In the activation range one can express the spectral transmittance as an activation curve:

$$D_A = D_A(\lambda)$$

In the bleaching range one can express the spectral transmittance as an absorption curve:

$$D_B = D_B(\lambda)$$

The bleaching effect at any wavelength will be proportional to the optical absorption at that wavelength.

In measuring spectral transmittance the probing beam should have minimal activation or bleaching effect on the film. The film, on the other hand, should have a strong effect on the probing beam. When there is a large difference in transparency between the bleached and activated (unbleached) portions of the film, a large signal-to-noise ratio (high contrast ratio) will result. This is important in detection of the optical signal.

Typically, the spectral absorbance is measured by passing light from a 1600 watt xenon arc lamp source through a monochromator. One then detects the change in film density with a radiometer.

Sensitivity of Optical Density to Energy Input

The sensitivity of a photochromic film to the radiant energy deposition is given by the functional relationship between D and the logarithm of the energy input E , where E is the optical power density in watts per cm^2 multiplied by the exposure time. Thus E is measured in joules per cm^2 . The slope of this curve is denoted by γ :

$$\gamma = \tan \alpha = \frac{\Delta D}{\Delta \log E}$$

In both the activation range and the absorption range, γ w 1 vary between 0.1 and 1, depending on the film and the wavelength.

Some typical photochromic film sensitivities can be cited as follows: For a 1 db change in optical density the energy density required is of the following order for the most sensitive films:

activation $\sim$ 3 to 15 $mj \ cm^{-2} \ db^{-1}$

bleaching $\sim$ 30 to 50 $mj \ cm^{-2} \ db^{-1}$

In comparison, conventional photographic film (ASA 32) requires 1 lumen m^{-2} for 0.25 sec to obtain 6 db. At   555 m μ 1 lumen m^{-2} is 0.161 microwatts per cm^2 . In 0.25 sec the energy deposition required is $4 \times 10^{-5} \ mj \ cm^{-2}$ for a 6 db change in optical density, as compared with 18 $mj \ cm^{-2}$ for photochromic film. Thus photochromic film is about 10^{-5} times less sensitive than conventional photographic film.

This lower sensitivity can be accepted however, for many optical recording applications because of the many advantages of photochromic film, specifically its reversibility and its high resolution. The important consideration is whether it is sufficiently sensitive for optical recording with available high resolution writing heads. Thus the matching of high resolution writing heads to the photochromic film sensitivity is the important recording criterion.

It is important to know the photochromic sensitivity to optical density change which can be easily measured. With a spectrometer one can easily distinguish an optical density change of

$$D = 0.02 \text{ db}$$

(The human eye sensitivity is 0.1 db.)

Thus, even if the energy density required for bleaching were 10 joules cm^{-2} db^{-1}, the sensitivity of the film for reading a bit would be only 1/50 of this or 0.2 joule per cm^2.

Reversibility, Spatial Resolution, Thermal Fading Rate

Photochromic films will have to be operated for hundreds of hours without degradation of properties. Hence, reversibility fatigue is a very important problem.

Spatial resolution of images appears to be much better than for conventional film, in which resolution is limited by grain size. In conventional film the limit of resolution is 100 to 500 lines per mm, equivalent to 1 to 10 microns. In photochromic film the limitation is molecular in size, of the order of 100 angstroms or 10^{-2} microns.

Thermal fading rates of minutes to hours have been observed at room temperatures for photochromic films, depending on the film. At refrigerated temperatures the thermal fading rate is much slower.

2.2 Luminescent Diode Writing Heads

Luminescent diode writing heads have a number of potential
advantages for recording on photographic film: The luminescent
P-N junction area can be in close contact with the film leading
to efficient utilization of the radiant energy. The radiant power
density produced by electrical pulses can be appreciable, of the
order of millijoules per cm^2 for short pulse lengths. The size
of the illuminated region can be a few square mils, small enough
to achieve a relatively high packing density of information on the
film without requiring optics. There is also the potentiality
that each diode will have a large operating range in which the
radiant energy output will be proportional to the current, making
it possible to operate it as an analogue recorder as well as a
digital recorder.

Another important consideration is the possibility of fabricating
luminescent diodes in array configuration. Since many recording
channels are required along the width of the film, a linear array
of diodes is needed. Neutron transmutation doping was selected as
a promising method for fabricating a luminescent diode array with
relatively close spacing in a single step. This doping method,
which is described in detail in Section 5, has the capability of
fabricating a linear array of P-N junctions of almost arbitrary
length, in a single semiconductor crystal, with a diode-to-diode
minimum spacing in the 10 to 30 mil range. Thus a 70 mm film width
(2800 mils) can potentially have 280 channels recorded on it with
a luminescent diode array produced by transmutation doping. One-
hundred channels should certainly be feasible. Such a luminescent
diode writing head array produced by transmutation doping is shown
schematically in Figure 2. Note that the P-N junctions produced by
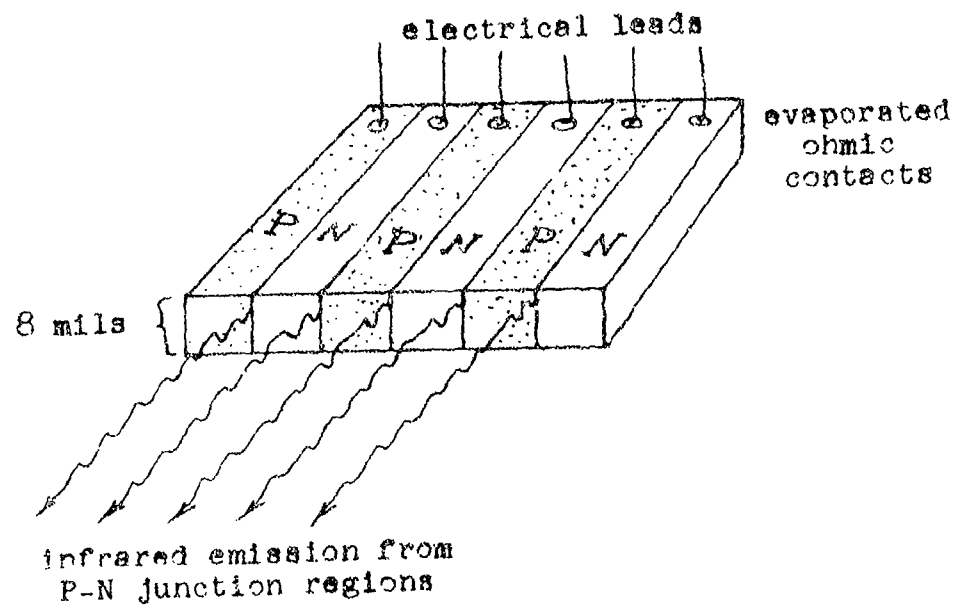transmutation are normal to the surface.

Figure 2.   Semiconductor Junction Array
Writing Head

2.3 Specifications for a Multiple Channel Recording System

The specifications for a multiple channel recording system include the following:

1. Number of channels:- Each channel will consist of a row of spots along the length of the film. Thus the number of channels must fit into the width of the film, which will be taken as either 35 mm or 70 mm.

2. Audio bandwidth per channel:- This will be a few thousand cycles per second.

3. Sampling rate per channel:- Each channel must be sampled one or more times per second for each cycle per second of bandwidth.

4. Film width

5. Film width per channel

6. Film speed

7. Spacing between time points on the film

8. Total recording time for the system using a single reel of photochromic film

9. Total length of film required for the total recording time

10. Number of repeated cyclings required for a 1200-foot reel

Ideal System

A set of ideal system specifications can be calculated for a 1200 channel system. A 6000 Hz bandwidth per channel is desired. If one samples the signal and records at a rate of 3 samples per Hz of bandwidth, this will lead to a sampling rate of 1800 per second per channel. On a 35 mm film this will lead to a width per channel of about 1 mil. At a spacing between time points of 1/3 mil this will require a film length per second of 18000 x 1/3 mil = 6 inches per second.

A total recording time of 30 days will be assumed for the use
period of the system with a 1200 foot reel of photochromic film.
This will require a total film length of 1.5 x 10^6 feet. The
1200 foot reel must therefore be re-used 1250 times in the course
of the 30 day period. This is almost attainable with one photo-
chromic material which was investigated.

Diode Array - Optimum Parameters

The best diode array which one can expect to fabricate
reliably by neutron transmutation techniques will have an inter-
diode spacing of 9 mils, giving a 300 channel array over the width
of a 70 mm photochromic film. The minimum spacing between diode
lines in the direction of film length will be set by the minimum
junction dimensions normal to the film, which are approximately
2 mils by 2 mils. If one selects a bandwidth per channel of
3000 Hz to be sampled twice per cycle per second, this gives a
sampling rate of 6000 per second per channel. For a spacing of
two mils between recording points the film speed per second must
be 6000 x 2 mils = 12 inches per second. For a 30 day period of
use one will therefore require a total film length of 3 x 10^6 feet.
The number of re-use cycles required for a 1200 foot reel of photo-
chromic film will therefore be 2500. This is at least 3 times
greater than the maximum number of cycles over which we could operate
the best photochromic material.

Diode Array - Achievable Parameters

We now consider a diode array fabricated by transmutation
doping whose properties are more representative of what can 1
achieved at present. The inter-junction spacing (width per channel)
is 27 mils leading to a 100 channel array for 70 mm photochromic
film. The spacing between recording points in the time-point
sequence on a channel will be taken as 8 mils, since this is the
width of the semiconductor wafer on which the diode array is doped.

Again we assume a bandwidth of 3000 Hz per channel, and if two time samples per Hz of bandwidth are recorded, one obtains a total of 6000 sample points per second in each channel. Since these sample points are 8 mils apart, one requires a film speed of 6000 x 8 mils or 48 inches per second. In a total use time of 30 days for the system this leads to a total film length of 12×10^6 feet. With a 1200 foot reel of film this requires that the film be re-used 10,000 times. Since the best photochromic material examined did not permit more than 800 cycles of re-use, it is clear that this system cannot be operated for the desired 30 day period with the available photochromic materials.

It appears likely however that in the future, inorganic photochromic materials will be available which will permit this number of re-uses. It is therefore of interest to point out (Section 2.4) some of the detailed considerations on which this analysis is based.

2.4 System Design of Recording Photochromic Film for
Optical Cross Correlator

In order to utilize photochromic films in an optical cross
correlator as a high-density recycleable memory, certain physical
conditions must be met. The density or total amount of information
that can be impressed upon the film must be sufficient to meet
overall system requirements. The sensitivity of the film to the
recording light must be sufficiently high to match the frequency
and power output of available activating and bleaching light
sources, and sufficiently insensitive to the reading light so that
the information may be transferred to the coherent light with
acceptable degradation. The lifetime or number of cycles of
activation, bleaching, and readout process is an important con-
sideration, perhaps the most critical. The various physical
requirements upon the photochromic film are not independent. The
sensitivity determines the ultraviolet exposure which therefore
will be shown to determine the degradation.

Other properties are likewise of importance. The thickness
of the film required to obtain the sensitivity limits the resolution
and therefore the information capacity of the film. The variation
of index of refraction with changes in optical density must be
minimal to avoid affecting the coherence properties of the laser
beam used for readout. Changes in index of refraction would require
the introduction of an index-matching liquid gate.

System Design as Related to the Photochromic Film

In the coherent optical cross correlator the photochromic
film which is the heart of the system, is involved in two steps:
a writing step and a readout step. The writing step puts the
information received by the overall system upon the film. The
reading step takes the information from the film and transfers it
to a coherent laser beam which subsequently performs the cross-
correlation procedure. These two steps involving the photochromic

film require three physical processes in the interaction of light and the photochromic material: 1) An activation process in which the photochromic molecules absorb an ultraviolet photon and become excited from a colorless-transparent to color-absorbing state. 2) A bleaching process in which the film is exposed to red or infrared and is returned to unexcited state. 3) The reading process in which the film is exposed to light at a wavelength which leaves the state of the photochromic molecule unaltered. These three processes determine the conditions under which the photochromic film operates. The order in time of these processes is determined by the system design and the light sources available.

In the system considered here, the film is activated first by ultraviolet and the information is then recorded through writing by means of bleaching. This mode is chosen since broad-area ultraviolet sources of any power output are available while point ultraviolet diodes do not exist. However, red light-emitting gallium arsenide phosphide diodes do exist.

It is seen from the experimental data discussed in Section 3 that the most serious limitation upon the system design is the degradation of the physical characteristics of the photochromic material itself in the course of normal operation. Both the photochromic properties and the transmission characteristics of the film are affected and one must design the system under those limitations. One must decide from such considerations whether in fact a system can be designed at all to satisfy the operating criteria for a particular purpose.

Photochromic Films

The system must go through the three stages of ultraviolet activation, bleaching by red light, reading by transmission of laser beam. For these steps to be carried out, the film must be transported from storage through the various optical steps to the second storage bin. When the film reaches the end of the roll, it may be rewound and started again or with appropriate mechanical

and optical alterations, the system can be operated in the reverse direction. The requirements upon the film velocity is determined by the requirements of the system and the physical properties of the film, and the properties of multi-element writing diodes. The reading operation and the ultraviolet activation introduce no further constraints upon the system. This arises since broad-area ultraviolet sources of nearly any power are available. The capacity of the laser likewise to transmit and receive information is much greater than required by system specifications.

The requirements of the system are discussed in the previous section. It is apparent from this analysis that reusing the film in successive runs is essential. Thus the lifetime, the number of cycles the film can go through while retaining the desired characteristics, becomes critically important.

In Section 3 we report the detailed measurements which we made on materials. However, the definition of a lifetime for the photochromic film is ambiguous, depending upon the history. The degradation of activity is apparently a function both of the total ultraviolet exposure and the state of activation of the material. This means that continuous ultraviolet exposure would lead to a shorter lifetime than determined through a cycling process of the ultraviolet exposure. Thus one ideally should determine the lifetime under the conditions set by the system.

We shall choose for reasons discussed below, a 3 db change in the density of the film. This choice is dictated by lifetime considerations. Thus a lifetime measurement should be one in which the ultraviolet exposure is sufficient to cause a 3 db change followed either by bleaching or thermal decay. Measurements upon VL316A laminated glass give a result of from 800 to 1200 cycles. The manufacturer reports that under similar conditions, 1800 cycles were achieved. For acrylic films the lifetimes were far less. We shall choose to consider 800 cycles as a reasonable estimate. This is less by a factor of 10 than the cycling capability required in Section 2.3.

It has been demonstrated that the glass laminate is greatly superior to the acrylic film. However, the use of glass laminate usually precludes the employment of a continuous strip reeled and unreeled as are the films. Glass laminate sheet could in principle be employed through the use of two right angle traversing mechanisms so that the entire surface is moved through the active area. This procedure is restricted by mechanical and space limitations. We therefore propose a method which could take advantage of both the properties of the glass and of the acrylic film. We suggest mounting the glass laminate upon flexible belts in sufficiently thin and small sections so that the belt could be driven exactly as would flexible film. The actual mechanical arrangement to insure proper transport between adjacent facets would introduce some complexity. Thus the longer lifetime of the glass laminate could be employed.

Since the degradation lifetime is so important, experiments have been conducted in this laboratory upon the possibility of increasing the lifetime for photochromic activity. It has been suggested that the longer lifetime for the glass laminate as compared to the acrylic film is due to oxygen being kept away from the photochromic molecules. A photochemical process involving oxygen in the presence of ultraviolet is a possible mechanism. Therefore a comparison of lifetime of photochromic acrylic films was made in normal atmosphere, vacuum conditions, and nitrogen atmosphere. The rather surprising result was found that the lifetime under the three conditions is the same. This may be due to one of two causes. Either oxygen does not affect the degradation or else oxygen was still supplied to the photochromic molecules through the action of the ultraviolet upon the solvent for the photochromic molecules or from the acrylic film itself.

Power Requirements for Writing Diode

We have determined for the VL316A glass that the power density
for a 1 db bleaching change for red light at 6000 Å is 14
millijoules/cm^2. For a spot size of area 20 square mils, an
energy of 17.5×10^{-4} millijoules is required, and for 300 channels
one therefore requires 5.2×10^{-4} joules per cycle. For 6000
repetitions per second one obtains about 3 watts of radiant power
required. Finally the maximum power for a 3 db change gives an
approximate upper limit of 9 watts.

Writing Mode

The writing mode requires that the photochromic material be
darkened by exposure to ultraviolet light to a desired density
and then transported to the writing station. The radiation from
the diode junction then bleaches the film. The amount of bleaching
that takes place depends upon the total energy delivered by the
diode. This will be proportional to the pulse height and duration,
the velocity of the film, the density to which the film has been
darkened, and the previous history of the photochromic film. The
amount of information required as well as the scattering and
background fluorescent light also affect the bleaching required.
In particular a requirement for ten levels of intensity per channel
sets up stringent considerations upon the intensities employed and
the allowable cross-talk and as well on the density and background
fluctuations. We have imposed the condition in order to allow
practical lifetime that the dynamic range between activation and
bleached densities should be no more than 3 db. This is to be
divided into ten levels, the intensity change is only 3 db so that
fluctuations in density or light intensity must be such as to give
a density of change in the film of no more than 7%. Thus the entire
process must be controlled to 7%. The entire process must be
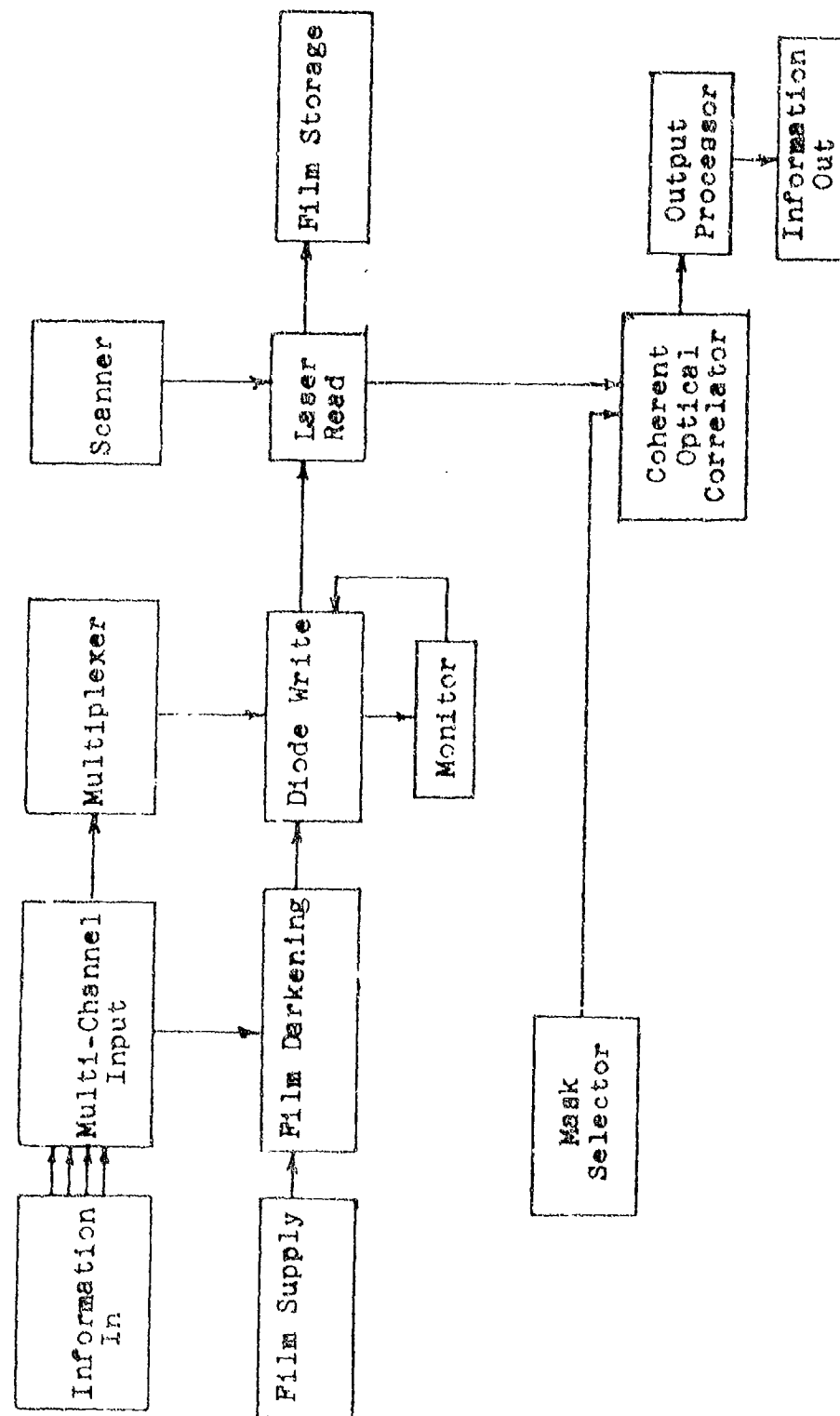monitored as shown in Figure 3.

Figure 3. Schematic System for Photochromic Writing

Digital representation in three channels splits the information into three parts with a 1 db change per level corresponding to a tolerance of fluctuations of 20%. Thus the stringency of the monitoring is greatly reduced. Since the bleaching does not affect the lifetime and the film is irradiated uniformly with ultraviolet, only one measurement is required to monitor the film rather than one at each channel. To ensure that the film returns to a uniform condition it may be necessary to have an auxiliary bleaching station before undergoing ultraviolet activation. This system requires also that the film properties are individually uniform over the active area.

Another consideration involved in the writing mode is the effect of the film motion upon the writing action. This is a function of both the film speed and the durations of the writing pulses. For a pulse of finite duration and a non-zero film velocity, the pulse would not produce a circular spot but a line of variable thickness and density. This may cause difficulty, especially since the pulse heights are varied. To minimize this effect offsetting the image may be useful. However the diode is to be operated in close proximity to the film for maximum effect so that offsetting may not be practicable. Keeping the pulse duration constant and varying only the height would give rise to relatively uniform shape so that it could be allowed for in the readout. An alternative method would be to bring the film to a stop before a pulse; this would add mechanical complications. Halation of the gaussian energy distributions across the diameter of the spot would result in the spot size increasing with beam intensity. This is unavoidable and must be considered in the readout. The effects of variations in spot size and shape with intensity must be investigated experimentally under operating conditions.

Activation Mode

The activations or darkening of the film is accomplished by uniform illumination by an ultraviolet long wave lamp through lenses and slits so that only the area corresponding to the image size of the multi-element diode is exposed. The density change as discussed above may require monitoring at the beginning and end of the process. Either the intensity of the ultraviolet lamp or the duration of the exposure may be controlled to exactly maintain the 3 db dynamic range independent of the history of the film.

Reading Mode

After the film is activated and written upon, it is transported to the reading station. The film is exposed to a laser beam of frequency about 5000 Å that does not bleach or activate. Two types of readout are possible. One is carried out by scanning the beam across the 300 channels so that the beam is modulated by the film. This modulated beam then transfers the information. The other method utilizes a spatially uniform laser beam and transmits a pattern of light and dark spots such that each channel is displayed simultaneously. The latter method would involve a mosaic of detectors as well as circuits adapted to simultaneous (as opposed to serial) transmission. This would require new techniques but permit greater use of the information capacity of the laser beam and may be of some future interest.

Conclusion

We have described a photochromic system which appears feasible for short operating periods of up to 30 hours. Longer periods would require increased lifetime for the photochromic material. The film suggested is VL316 or equivalent, This material is available only as a glass laminate, which might for example be mounted in narrow strips on a flexible belt to approximate the handling ease which is characteristic of roll films. Further

investigation should be directed to determination of factors
which affect lifetime of the photochromic material. It has been
suggested for example that oxygen may be responsible for shortened
lifetime. Discovery and removal of such factors could lead to a
system with extended operating lifetime.

SECTION 3
Photochromic Materials Assessment

The important characteristics of photochromic material are
1) its reversibility, 2) its spectral range, 3) the energy
density required for bleaching and 4) its expected lifetime in
cycles of use. A program of measurements was carried out on a
number of available photochromic materials to determine these
characteristics. The measurements and results are described in
this section.

Photochromic material measurements are described in Section
3.1. The results are summarized in Section 3.2. It was found
that only one available material had the spectral range and low
energy density for bleaching that is at all compatible with
luminescent diodes. It was also found that the lifetime in
use cycles of the system is relatively limited.

The lifetime of the photochromic film is limited by the
deterioration of the chemical compound in the ultraviolet activation
process. Bleaching and reading do not lead to the aging effect.
Deterioration of the photochromic material is observed as a residual
darkening of the film, not removable through the bleaching process
and apparently permanent. As the deterioration proceeds, more
ultraviolet light is required to produce a given density change.
Eventually the film is no longer sensitive to either activation or
bleaching light. Since the deterioration is proportional to the
ultraviolet exposure, the minimum exposure compatible with the
operating condition of the system is desirable. We have selected
a 3 db dynamic range for our system considerations. Measurements
on the UL316A film (the most satisfactory) both for laminated and
acrylic films indicate an expected lifetime of 800 cycles. This
means that the film in our system can be cycled through activation,
bleaching, and reading for 800 repetitions while retaining the 3 db
dynamic range.

Because of the importance of the limited lifetime of the film,
an experimental investigation was made of the possibility of
increasing this lifetime by changing the chemical environment of
the photochromic material during the activation. This is described
in Section 3.3.

3.1 Photochromic Materials Measurement Methods

Qualitative and quantitative measurements have been carried out to investigate the photochromic effect on various films as a function of wavelength. The properties of interest are the behavior with intensity at the wavelengths of activation, bleaching, and non-destructive readout. The activating wavelengths are in the ultraviolet and are supplied by a low pressure mercury lamp, Spectralight Black Light, filtered to give only long wave ultraviolet transmitted through the glass. The bleaching wavelengths which have been studied range from 575 m micron (center frequency) to .900 m micron. The desired wavelengths for bleaching are in the infrared from 600 to 900 m micron. (These wavelengths are emitted by gallium arsenide, gallium phosphide, or gallium arsenide-phosphide light-emitting diodes.)

The photochromic films investigated are supplied by American Cyanamid and Vari-Light. The American Cyanimid types 43-540, 43-540A, 51-142, and 63-071 are polyester films coated on one surface by a photochromic compound. The Vari-Light types UL-204A and UL-316A are supplied as laminated glass with the coated film mounted between the laminations which do not interfere with the ultraviolet activation.

Experimental Procedure

The films were activated through exposure to the Spectraline ultraviolet lamp. The exposures were for two minutes, which was a sufficient time to produce saturation as determined through removal of all detail produced by previous bleaching.

Bleaching was produced through two distinct experimental arrangements:

1. Direct illumination from the lamp through a red filter. The lamps used were the Bausch and Lomb Microscope Lamp with tungsten bulb or the Sylvania Movielight Sun Gun II. The light was filtered with a Tiffen Photar No. 25 (Red 1, Series C color correction) filter. The light was focussed upon the film by a lens. This arrangement possesses the advantage of permitting high intensities over a wide range of wavelengths. The filter essentially absorbs in the blue end of the spectrum while transmitting the red-yellow.

2. To investigate the wavelength dependence of the bleaching process, the Jarrell-Ash grating monochromator 82-421 is employed, with f/3.6 and a dispersion of 33 Å/mm. The photochromic film is placed at the exit slit of the monochromator. Since the intensity of the light available at the exit aperture of the monochromator is extremely small as compared to direct exposure, only the Sylvania Sun Gun with a focussing lens was employed. Also, the entrance slit of the monochromator was removed, reducing the wavelength resolution of the monochromator. Long exposure times are required. The red color correction filter is placed before the entrance aperture to remove the second order spectra of the blue light. The experimental setup is shown in Figure 4. Since the entrance slit is removed, the wavelength spread at the exit slit is approximately 300 Å as calculated from the characteristics furnished by the manufacturer of the monochromator.

Power Measurements

The relative power is measured by an International Light Corp. IL600 photometer with a vacuum photo-diode calibrated so that the response at 910 m microns is known to be 174 microwatts per cm^2 per microamp of photometer reading. A calibrated relative spectral response curve is furnished with the device.
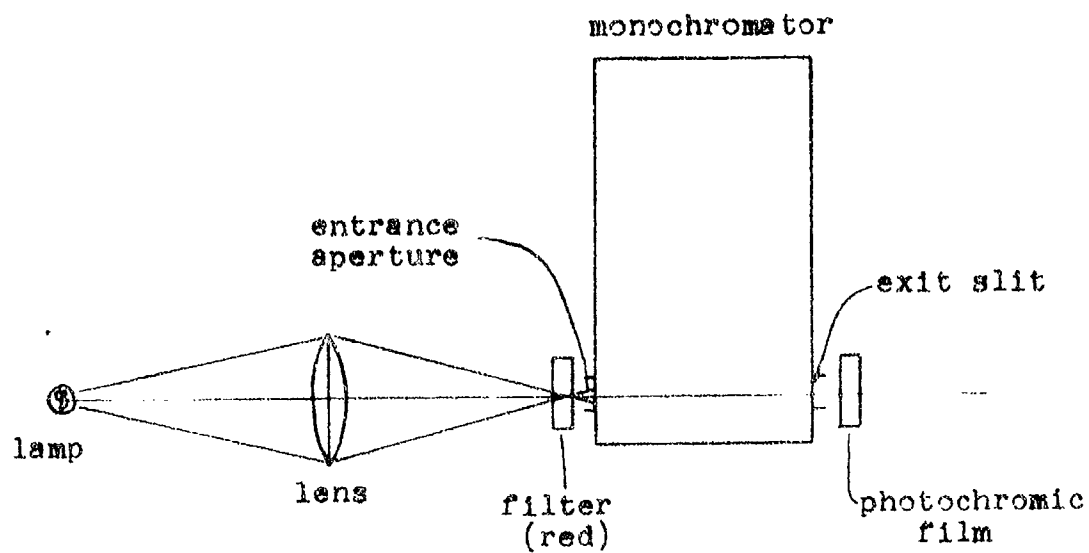
Figure 4.   Schematic Test Setup for
             Photochromic Film

Detailed results of the measurements on the various photo-
chromic films are given in Section 3.2.

Observations and Techniques

A series of measurements was carried out with American Cyanamid
films 63-071, 51-142, 43-540, and 43-540A. The first film samples
had been stored for approximately four months before any extensive
testing. The responses of the samples to bleaching and activation
differed widely with respect to each other and with the curves
supplied by the manufacturer. Although bleaching was observed,
it was noted only at high light intensities with the Sylvania
Sun Gun II. The conclusion to be drawn here is that the samples
of the films used were unstable with respect to time, i.e., shelf
life is limited.

Film freshly arrived from the manufacturer was tested. All
demonstrated bleaching effects with the Bausch and Lomb Microscope
Lamp. However, 43-540A showed bleaching effects with white light
as well as with red. The contrast due to bleaching was noted to
remain after days in darkness. The best response was shown by
film type 51-142.

Further investigation of bleaching was carried out with
the monochromator. In order to obtain sufficient intensity in
a spectral line, the entrance slit to the monochromator was removed
while the exit slit was replaced by a longer slit. Since the
aperture was open the wavelength focussed on the plane of the exit
aperture. The band of wavelengths about the center is approximately
300 Å or 30 m microns. The red filter was used over the entrance
aperture to eliminate effects from higher order spectra. Bleaching
measurements were carried out on American Cyanamid's film type 51-142
at various wavelengths and varying times of exposure (up to 1 hour).
For exposures longer than 1 hour, heating problems develop in the
monochromator which then requires shielding. Wavelengths studied
were 575, 600, 650, 700, 800, and 900 m microns.

The relative power impinging on the film through the mono-
chromator at settings of 575 and 900 m microns were measured by
the photometer, taking into account the response curve of the
vacuum photo diode. This gives the expression

$$\text{Power Ratio } \frac{900 \text{ m}\mu}{575 \text{ m}\mu} = \frac{\text{photometer reading at } 900}{\text{photometer reading at } 575} \times \frac{\text{sensitivity at } 575}{\text{sensitivity at } 900}$$

This ratio was found to be 1.77. The power at 900 is therefore
almost double that at 575. The exposure time to obtain approxi-
mately 3 db of density change at 575 is 30 minutes. When no
bleaching was observed after 1 hour exposure at 900 m μ, one
could conclude that the power required for bleaching is greater
than four times that at 575. (The manufacturer gives a figure of
4 joules/cm^2 for bleaching at 575 so that the conclusion is
drawn that the power required at 900 m μ is greater than
16 joules/cm^2.

Thus we have se. an approximate lower limit of 16 joules/cm^2
for bleaching at 900 mm with a similar figure for the wavelengths
from 650 to 900 m μ .

4.' Properties of Various Photochromic Films

Vari Light VL-316A Laminated Glass

Activation: On ultraviolet activation, the film changes from
colorless to purple. The activation decays within 30 minutes
after which it is insensitive to bleaching. However, its
residual color, a reddish hue, remains for over 72 hours.

Bleaching: Bleaching occurs at 575 to 600 mμ . At 600 mμ
a 1 db change requires an energy density of about 15 millijoules
per cm^2. Strong bleaching takes place up to 650 mμ , but no
bleaching is observed at 660 mμ . None is observed from 700
to 900 mμ .

The decay of sensitivity to bleaching is fairly rapid.
After 30 minutes from time of ultraviolet activation, the bleaching
effect is small even though the color remains. This gives rise to
a failure of reciprocity and indicates that an improvement of
sensitivity should arise when pulsed diodes are to be used
immediately after activation.

The material fluoresces under ultraviolet. This orange
fluorescence is an indication of sensitivity to bleaching. One
sample became inactive after several cycles and a period of
storage and likewise ceased to fluoresce.

This film type appears to be most suitable of all photochromic
materials tested.

<u>Vari-Light VL-204 Laminated Glass</u>

Activation: Color changes upon ultraviolet excitation from yellow
     to gray-black.

Bleaching: Shows no sign of bleaching at any wavelength.

     The two samples tested varied widely in characteristics.
One faded almost immediately upon activation either by ultraviolet
or visible light, so it was impossible to determine if bleaching
occurred.   The other sample remained activated long enough to show
that no bleaching occurred.   One sample became inactive after some
tests and storage time.

     This material is not suitable.

<u>American Cyanamid 51-142</u>

Activation: Upon ultraviolet exposure, color changed from
     colorless to dark blue.

Bleaching: Bleaching takes place from 575 to 600 mμ .   At
     600 mμ a 3 db change required 13.5 joules/cm^2.   Between
     600 and 650 mμ bleaching occurred, falling off with
     increasing wavelength.   No bleaching occurred from 700 to
     900 mμ .

     The film   retains sensitivity to bleaching at times greater
than 1 hour from time of activation.   The film suffers irreversible
change after exposure to intense visible light.   It also loses
sensitivity for activating and bleaching processes after cyclic
tests, retaining a permanent bluish color.

     This film has bleaching properties above 600 mμ but
requires too high power densities to be useful.

American Cyanamid 43-540<u>s</u>

Activation: Upon ultraviolet exposure, color changed from
colorless to purple.

Bleaching: From 575 to 600 mμ the film is sensitive to bleaching.
At 600 mμ for a 3 db change 13.5 Joules/cm^2 is required.
Between 600 and 650 mμ bleaching occurs, falling off with
increasing wavelength. Between 700 and 900 mμ no bleaching
occurs.

The film becomes insensitive within 30 minutes after activation.
Under ultraviolet exposure, dark red fluorescence occurs. When the
activation properties of the film are destroyed, the fluorescence
is weak or non-existent. One sample had no response to ultraviolet
after one month of storage.

This film bleaches above 600 mμ but requires to high
power densities for bleaching to be useful.

American Cyanamid 43-540

Activation: Upon ultraviolet exposure, color changes from light
yellow to red-orange.

Bleaching: No bleaching was observed.

This film loses sensitivity to activation after either storage
or activation cycles. It retains orange coloration permanently.

This film is not suitable since no bleaching was observed.

American Cyanamid 63-071

Activation: Upon ultraviolet exposure, the film color changes
     from yellow to blue-gray.

Bleaching: From 575 to 60 mμ faint bleaching takes place.
     At 575 mμ for a change of approximately 3 db, 20 joules/cm^2
     is required. From 650 to 900 mμ no bleaching was observed.

          This film showed diminished activation properties with storage.
Its bleaching action is weak. The material is considered
unsatisfactory.

Conclusions

          The conclusion drawn from the measurements discussed above
is the following: The Vari-Light type VL316A laminated glass
material appears to be moderately promising in conjunction with
the proposed use of gallium arsenide phosphide diodes having a
frequency of emission varying from 600 mμ to 70 mμ .

3.3 Study of Ultraviolet Deterioration of Photochromic Activity
in Air, Nitrogen, and Vacuum Environments

It has been suggested that the deterioration of photochromic activity in various films we have tested may be due to a photochemical process involving the oxidation of the molecule in the presence of an ultraviolet photon. In order to examine this, we investigated the degradation lifetime of the photochromic material under air, dry nitrogen, and vacuum conditions to determine whether the useful lifetime of the   terial can be significantly extended by changing operating envi   ments. The principal material of interest in these tests was the Vari-Light type VL316A material, since it is the most suitable photochromic for this application.

. order to determine the effect of the various environments upon the lifetime of the photochromic activity, two experimental methods were used. In the first method the change in transmission as a function of the total ultraviolet exposure time was measured. That is, the percentage change in transmission due to ultraviolet activation from the completely bleached state was measured after fixed periods of ultraviolet exposure at constant levels of intensity. The sequence of activation and bleaching by infrared or by decay is required. The film suffers an irreversible darkening with ultraviolet exposure which was connected with the loss of activity.

The second method, which proved superior in practice, consisted of visual observation of the activation of the photochromic material through its fluorescence rather than through changes in transmission. We have observed that in the VL316A photochromic material there is a strong red fluorescence associated with the optical activity of the film under ultraviolet exposure, which is

presumably due to the activated molecules. When all traces of this fluorescence is gone the film is unable to be activated at any intensity of ultraviolet. Thus, observing this fluorescence permits the continuous observation of the optical activity of the film.

First Method

The experimental design for the first method is shown in Figure 5. The lamp is a collimated tungsten source. The glass filters (Corning) function to remove the bleaching or activating elements from the tungsten lamp light. The chemical dessicator is of thick-walled pyrex with a single pumping lead-through. The ultraviolet lamp is a Spectraline Blacklight long wave type. The detector is the International Light IL600 photometer.

The experimental procedure was to measure the transmission of the sample – VL316A acrylic film – then exposing the sample to ultraviolet for a fixed period of time at a fixed intensity level, then measuring again for transmission. Finally the activity of the film was permitted to decay or undergo a bleaching process and the transmission was determined again. This was done for air, vacuum (100-200 microns) and nitrogen.

Results were not entirely conclusive. This was due to the great reduction of ultraviolet transmission through the pyrex enclosure, to the bleaching and activating effects of the tungsten light which were not completely suppressed by the filter, by the low intensities of the tungsten light which resulted from the use of the filter, and to the geometry involved. However, no substantial change in the activity lifetime of the photochromic film was noted under the various conditions of environment.
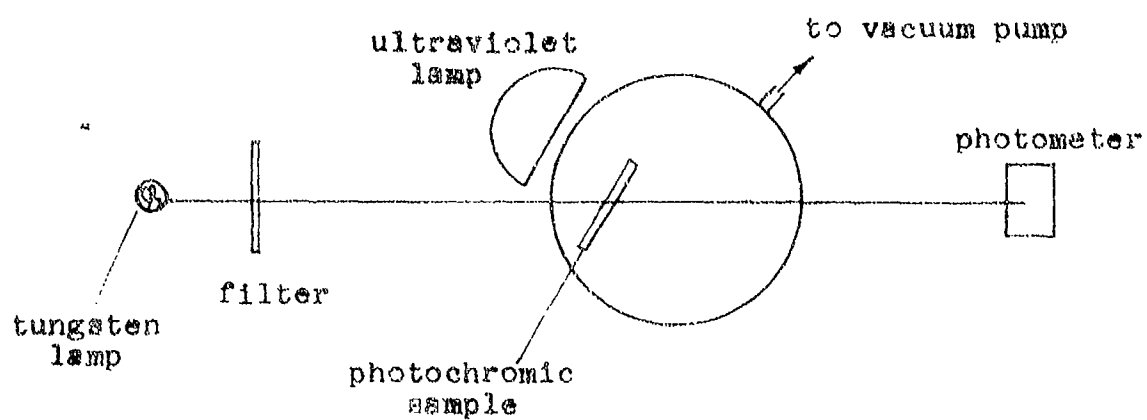
Figure 5.   Experimental Setup for Photochromic Film
Lifetime Measurement

Second Method

The conditions under which the experiments were conducted
were as follows. Identical samples of the VL316A film were
prepared and mounted in the dessicator. Alternate pairs of life
tests were made in air and vacuum, air and nitrogen. The vacuum
conditions were produced by a mechanical forepump in the range of
100-200 microns. Before exposure to ultraviolet, the dessicator
with the sample was pumped down to its final pressure and kept
under vacuum for 1 hour. In one trial the sample was left for
36 hours at 100 microns. The nitrogen atmosphere was produced
by pumping the dessicator down to 1000 microns using a small
Fisher vacuum system, filling it with dry nitrogen, then pumping
down again. This flushing, filling and pumping was repeated
10 times. At the end of the flushing process the sample was
left in the nitrogen atmosphere for 1 hour. It was then pumped
down and filled with nitrogen to approximately atmospheric
pressure. At this point the ultraviolet was turned on and the
life test begun.

Conclusions

No observable difference was noted and one must conclude that
the deterioration is independent of whether the activation is
performed in air, nitrogen, or vacuum. Nevertheless, to definitely
establish the effect, one should perhaps fabricate the photochromic
chemical and film together in the proper atmosphere.

SECTION 4

Power Compatibility of Semiconductor
Diodes With Photochromic Films

It is pointed out in Section 3 that the bleaching mode in photochromic films requires radiation in the 5000 to 7000 angstrom range. It is also necessary to achieve an energy density of the order of 10 millijoules per cm^2 to obtain bleaching. In this section we consider the attainability of this wavelength and energy density with semiconductor luminescent diode arrays which can be fabricated by transmutation.

Gallium arsenide phosphide can be produced to emit at any wavelength in the range from about 5900 Å to 9100 Å depending on its composition. Gallium phosphide emits in the green, while gallium arsenide emits in the infrared. Let x denote the fraction of arsenic atoms in gallium arsenide which are replaced by phosphorus to produce a 3-5 semiconductor crystal denoted by GaP_xAs_{1-x}. Then the wavelength corresponding to the emission peak varies with x approximately as shown in Table 1. Hence by selecting the initial crystal composition appropriately one can obtain the luminescent emission peak at the desired wavelength in the range from 5900 to 9100 angstroms. This is discussed in detail by Gershenzon.[1] From $x = 0$ to $x = 0.4$ the mechanism for luminescence proceeds via a direct bandgap transition, $k = (0,0,0)$ bandgap edge, while from $x = 0.4$ to $x = 1.0$ the luminescence proceeds via an indirect bandgap transition $k = (1,0,0)$ bandgap edge.

Any semiconductor composition in the family GaP_xAs_{1-x} can be doped in a junction array configuration by neutron transmutation techniques. At the beginning of this investigation it was intended to select a composition that is compatible in frequency with a

Table 1

Estimated Wavelength of Emission Peak versus
Composition for Gallium Arsenide Phosphide

Fraction of As Atoms Replaced by P Atoms	Energy of Emission Peak (Angstroms)
0	9100
0.1	8550
0.2	8000
0.3	7450
0.4	7000
0.5	6800
0.6	6650
0.7	6500
0.8	6350
0.9	6100
1.0	5900

Note: These values correspond to room temperature.
In most cases they are estimated values rather
than actually observed values.

satisfactory photochromic material. When it was found that no
photochromic material had a sufficiently long life cycle to
satisfy the system requirements, it was decided to conduct the
power compatibility measurements with the most convenient and
most easily obtainable semiconductor material in this family,
gallium arsenide.

Power Density Obtainable from Diodes

It is important to determine the power density compability
of luminescent diodes with photochromic films. In order to do
this, one must first measure the power density obtainable from
both conventional (diffused) diodes and from transmutation diodes.
For the reason cited above, the measurements were made for gallium
arsenide luminescent diodes. An IL600 photometer with a PT-200A
phototube (vacuum photo diode) with an S-1 spectral response
was used as the sensing head. Typical data for the conventional
diode and for the transmutation diode are given as follows:

The diffusion diode at 100 milliamperes produced a power
density of 1.43 microwatts per cm^2 at a distance of 5.8 cm.
This corresponds to a total infrared output of 6×10^{-4} watts at
the surface. The emitting area is about 1600 square mils. This
corresponds to an optical power density of

$$P = \frac{6 \times 10^{-4} \text{ watts}}{10^{-2} \text{ cm}^2} = 60 \text{ milliwatts per } cm^2$$

The efficiency of this diode was about 0.1% in terms of
optical power out per electrical power in.

The transmutation junction at 100 milliamperes produced 9×10^{-6} watts of infrared power at the surface. Its effective emitting area was 8 mils by 2 mils to give 16 square mils or 10^{-4} cm^2. Hence its power density was

$$P = \frac{9 \times 10^{-6} \text{ watts}}{10^{-4} \text{ } cm^2} = 90 \text{ milliwatts per } cm^2$$

Its efficiency was about 1/15 that of the diffusion diode. This is due to its greater electrical resistance by about this same factor.

Now the minimum energy density required for photochromic bleaching (at the appropriate bleaching frequency) is about 10 to 20 millijoules per cm^2. From this one would conclude that at the power densities measured for the luminescent diodes one would require at least a 0.1 second exposure in order to write on the photochromic film. However, under pulsed operation the exposure time can be greatly reduced, as pointed out in Sections 5 and 7.

SECTION 5
Application of Neutron Transmutation Techniques

Neutron transmutation techniques can make a significant
contribution in the development of multi-channel recording on
photochromic film by means of its capability for fabricating a
high linear density of diodes on a single wafer of semiconductor,
each diode having a small emitting area. An array of 100 diodes
over a 1 inch width of semiconductor wafer is an attainable
objective. This corresponds to a 10 mil spacing between diodes,
each diode having a radiation-emitting area of 5 to 10 square
mils. In the present program the more modest objective of a
30-mil diode spacing was set. This goal was attained and a four
diode array with 30-mil spacing was made. The radiation-emitting
area of each diode was 15 square mils.

Transmutation techniques have thus been used in this work to
make an integrated linear optical array fabricated on a single
monolithic slice of gallium arsenide. This integrated device
includes all electrical connection points and all infrared-emitting
junctions. Furthermore, we have shown that despite the small size
and compactness of the diode array, a sufficient intensity for
film recording is available from each P-N junction element.

Such a high linear density diode array must be conformable
with an erasible (re-useable) photochromic film strip if a recor-
ding system suitable for optical computer applications is to be
operated. This involves matching of (a) the spectral character-
istics of the film and (b) the energy sensitivity of the film,
to semiconductor photodiode arrays. A number of semiconductors
with a variety of spectral characteristics are available for
doping in high density arrays by transmutation techniques. These
semiconductors include gallium arsenide (infrared) gallium

Table 2

Transmutation Mechanisms in Gallium Arsenide

Isotope	Percentage Natural Abundance	Microscopic Absorption Cross-Section (barns)	Macroscopic Absorption Cross-Section (cm^{-1})
Ga-69	60%	1.4	0.016
Ga-71	40%	4.0	0.035
As-75	100%	4.4	0.10

	Reaction	Half-Life
Ga-69	Ga^{69} - - - - - Ga^{70}	$\dfrac{20\ min}{\beta^-}$ - - - - - Ge^{70}
Ga-71	Ga^{71} - - - - - Ga^{72}	$\dfrac{14.2\ hr}{\beta^-}$ - - - - - Ge^{72}
As-75	As^{75} - - - - - As^{76}	$\dfrac{27\ hr}{\beta^-}$ - - - - - Se^{76}

Note that a thermal nvt of 10^{19} neutrons per cm^2 would produce a concentration of 1.0×10^{18} selenium impurities per cm^3, and 3.1×10^{17} atoms per cm^3 of germanium.

Table 3

Transmutation Mechanisms in Gallium Phosphide

Isotope	Percentage Natural Abundance	Microscopic Absorption Cross-Section (barns)	Macroscopic Absorption Cross-Section (cm^{-1})
Ga-69	60%	1.4	0.016
Ga-71	40%	4.0	0.035
P-31	100%	0.20	0.0045

	Reaction	Half-Life
Ga-69	$Ga^{69} \relbar\joinrel\relbar Ga^{70} \relbar\joinrel\relbar \frac{20\ min}{\beta^-} \relbar\joinrel\relbar Ge^{70}$	
Ga-71	$Ga^{71} \relbar\joinrel\relbar Ga^{72} \relbar\joinrel\relbar \frac{14.2\ hr}{\beta^-} \relbar\joinrel\relbar Ge^{72}$	
P-31	$P^{31} \relbar\joinrel\relbar P^{32} \relbar\joinrel\relbar \frac{14.2\ days}{\beta^-} \relbar\joinrel\relbar S^{32}$	

Gershenzon[5] gives experimental data to confirm
that sulfur is a donor in gallium phosphide.

arsenide phosphide (in the red) and gallium phosphide (red to green depending on the doping), in which transmutation doping has been demonstrated.

Transmutation doping can be used to make optical-emitting arrays in a number of other materials in addition to gallium arsenide. These include gallium arsenide phosphide and gallium phosphide, both of which produce visible radiation. Table 2 lists the transmutation doping nuclear reactions in gallium arsenide. Table 3 lists the transmutation doping nuclear reactions in gallium phosphide. These tables show the nuclear reactions and the nuclear cross sections as well as the final transmutation doping products. Gallium arsenide phosphide has the transmutation reactions and dopant products shown in both tables. The nuclear cross sections are obtained by linear combination of the values in the two tables, depending on the phosphide composition of the crystal.

Principles of Neutron Transmutation Doping

A brief summary of neutron transmutation doping technology will be given here as it applies to gallium arsenide. It will be analogous for other gallium compound semiconductors. The principles of transmutation doping are described in References 2, 3, and 4 of the bibliography to this report.

The technology of transmutation doping may be briefly summarized under the following headings:

1. Radiation dies

2. Radiation capsule

3. Relation between initial semiconductor resistivity and neutron exposure required

4. Annealing procedure

5. Geometry of the doped regions.

Radiation Dies

Radiation dies are thin enclosures of cadmium within which the semiconductor specimens are contained during irradiation. Cadmium is a strong absorber of thermal neutrons and even a thin layer (e.g. five to ten mils thick) of cadmium can exclude most of t'e thermal neutron flux. A pattern of slits is fabricated in the cadmium by photoresist or metal stamping techniques. Thermal neutrons can then enter the semiconductor only through the slits. The spatial pattern of transmutation doping in the semiconductor is therefore controlled by the slit pattern in the radiation die.

Mechanically, the radiation die consists of cadmium bonded to a copper or steel substrate for strength and rigidity. Copper and steel are transparent to neutrons.

Radiation Capsule

This is a steel box (e.g. 3" by 1" by 7") in which many radiation die units (each consisting of the radiation die, the semiconductor material, and holding frames) are packed. The capsule is then inserted into a nuclear reactor for irradiation. Our gallium arsenide irradiations have averaged 4 to 6 days, corresponding to about 10^{19} nvt.

Final Resistivity and Required Neutron Exposure

From the nuclear properties of gallium arsenide one can show that each unit of nvt leads to about 0.1 N type impurity inserted. In a uniformly irradiated specimen the final N type concentration C_N is given by

$$C_N = 0.1 \ (nvt) - C_P$$

where C_P is the initial P type concentration. The concentrations are determined by the semiconductor conductivity and mobility. (These are usually measured by Hall effect and resistivity measurements using the Van der Pauw technique.) As an example, if C_P is initially 3×10^{17} P type and the nvt is 10^{19}, C_N will be 7×10^{17} N type. This determines the final resistivity.

In a non-uniformly irradiated specimen, i.e. within a radiation die with a slit pattern, the important parameter is the ratio B/A, where

$$\frac{B}{A} = \frac{\text{Transmutations Under Die}}{\text{Transmutations Under Slit}}$$

This usually ranges from 0.5 to 0.1, depending on the slit geometry.

One can then set up expressions for calculating C_N under the die and under the slit which will depend on the spatial distribution of the flux and on the slit geometry. One wants a change in semiconductor type (P to N type) under the slit, and no change in type under the die. Such detailed calculations will be presented for gallium arsenide in the next section.

Annealing Procedure

After irradiation the gallium arsenide is intrinsic (very high resistivity) because of radiation damage defects. These defects are next removed by annealing, leaving only the transmutation-induced concentration, in addition to the initial doping. The annealing is done in an atmosphere of arsenic at temperatures of 600° C to 800° C for a short time period.

5.1 Design Considerations in Fabricating an Optical Array in Transmutable Semiconductors

The following considerations apply to any semiconductor, in particular to gallium compound semiconductors, which can be doped by transmutation. In order to present the discussion in concrete terms however, we shall speak specifically of gallium arsenide. The reader will realize that the design considerations can be directly recast in terms of each of the semiconductors previously enumerated.

Similarly we shall speak specifically of infrared radiation which is produced by gallium arsenide. It will be understood that visible optical radiation in the green to red range will be produced by the other semiconductors.

It will be assumed that a clear-through doping configuration produced by neutron transmutation techniques will be formed in gallium arsenide. The gallium arsenide will initially be P type of some specified resistivity. It will be irradiated for a certain nvt (neutron exposure, neutron density times velocity times t) through a radiation die of specified pattern. Thus the principal process variables are

1) initial resistivity of gallium arsenide
2) nvt exposure
3) radiation die pattern.

The effects of the process variables on the geometric and optical parameters of the array, which determine its infrared emitting characteristics, are one major area in device design. The second major area is that of electrical and thermal response of the array, including the problems of 1) attachment of electrical

connections,   2) encapsulation and heat dissipation considerations and   3) mechanical design of the writing heads. The geometric and optical parameters will be discussed in this section, while the other irradiation techniques and semiconductor processing techniques will be discussed in the next section.

Major emphasis in this program has been placed on the first area: the effects of the transmutation doping process variables on the parameters of the diode array. The following parameters of the array are important in determining its infrared recording characteristics:

1. Dimensions and form of the emitting P-N junction
   regions in each diode recording channel

2. Spacing between diodes or recording channels

3. Intensity of the infrared emission from the
   individual diodes

It is important to set forth the design possibilities in each of these areas and to consider their implications in terms of the transmutation doping process variables.

Dimensions and Form of Doped Regions

Some typical doping patterns which can be considered for a linear diode array are shown in Figure   6.

Pattern 1   shows alternate stripes of P and N type regions
             normal to the surface and extending clear-through
             the slice

Pattern 2   shows rectangular isolated N type regions normal
             to the surface (and extending clear-through the
             slice) within a P type bulk which is held at a
             common electrical potential. The dimensions of
             the isolated N type regions may be selected, e.g.,
             they can be squares. Alternatively, the bulk
             region can be N type with the isolated regions
             P type.

Pattern 1
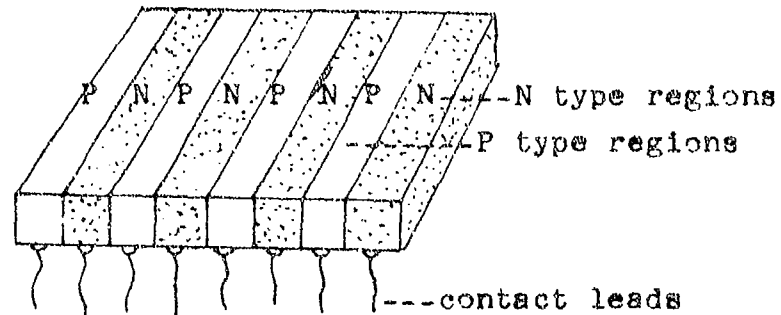
Alternate Stripe Configuration

Pattern 2
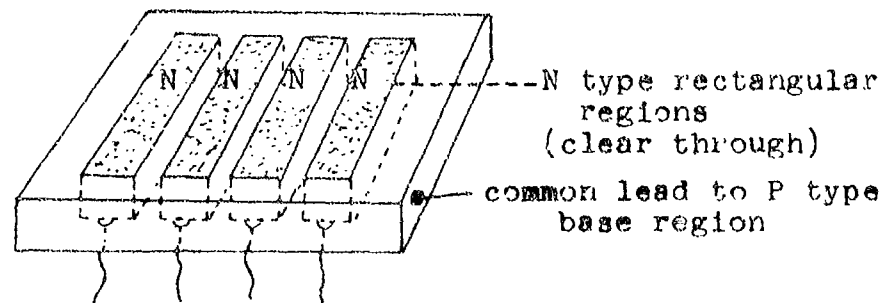
Rectangular Isolated Regions

Figure 6. Transmutation Doping Patterns for Diode Arrays

In Pattern 1 each junction stripe (the boundary line between an N and a P type region) represents a writing head. The writing head is excited by placing an adequate forward bias across this individual junction. Note that each junction is electrically isolated from all other junctions, and can therefore be separately excited. If each region is 30 mils wide (a reasonable width) a total of 33 junctions would be present per inch to serve as writing heads.

In Pattern 2 the bulk P type semiconductor would be held at a common potential. Each isolated N type region would be reverse biased relative to the bulk material in the no-write mode, and forward biased in the write-mode, i.e., when infrared emission takes place. However, this pattern requires two P-N junctions - those surrounding an N type region - per bit. Therefore this pattern is less useful and the first pattern will be used.

Figure 2 shows the use of a Pattern 1 doping configuration as an array of writing heads.

Spacing Between Diodes on Recording Channels

The minimum spacing attainable between recording channels will depend on two considerations:

1. the resolution of doped regions attainable by transmutation techniques in gallium arsenide

2. the effect of diode dimensions and spacing on obtaining adequate infrared power emission for film recording

The problems of obtaining high resolution between doped regions in a reproducible manner depends on a number of factors:

(1) Inhomogeneities in the initial nominal doping of the
gallium arsenide. A 10% random variation in the doping
can easily be tolerated. However, depending upon the
source of the initial P type material, a considerably
higher doping variation may be present in nominally
homogeneous gallium arsenide, since the purification and
crystal growth technology has not yet approached that of
silicon and germanium. Compensating techniques can be
used in the transmutation doping process. These will be
described.

(2) Microscopic spatial variation of the neutron flux pattern
across the radiation die. This spatial variation is con-
siderably affected by the radiation die pattern. It can
be analytically predicted and experimentally observed.

(3) Spatial resolution obtainable in fabrication of radiation
dies. This resolution can be obtained in the range of
10 mils. However, careful and painstaking techniques are
necessary for consistently reproducible results in the
radiation die pattern. Even a 30 mil pattern in a cadmium
radiation die requires a considerable development effort
for consistent results. We have obtained multiple doped
regions separated by 30 mils by welding a composite
radiation die of cadmium and steel as discussed in Section
5.2.

(4) Attachment of electrical contacts to the gallium arsenide
doped regions. The following two-step method has proven
most useful for contact attachment:

  a. Evaporation of indium alloys to the contact areas.
     This evaporation takes place through a photo-etched
     metal mask. Indium-zinc is used for contacts to
     P type regions, indium-tin for contacts to N type
     regions.

  b. Use of a nailhead-bonder (Kulicke & Soffa) for small
     area contacts to the evaporated alloy contacts.

A more detailed description is given in Section 5.2.

Intensity of Infrared Emission

It has been shown by the experiments described in Section 3 that a minimum energy density of 10 to 20 millijoules per cm^2 is necessary for bleaching of the most sensitive photochromic material available to us. It has been shown in Section 4 that typical gallium arsenide transmutation diodes produced energy densities of the order of 100 millijoules per cm^2 in one second. On the basis of this data one can predict that if similar energy densities could be produced at the required bleaching wavelength (550 to 650 mμ) one could bleach an appropriate photochromic material with a pulse whose width is 0.1 millisecond to 1 millisecond. The detailed energy balance can be made as follows: (It should be remembered that this calculation assumes that a gallium arsenide phosphide diode can yield the same luminescent power as a gallium arsenide diode):

The efficiency of a gallium arsenide transmutation diode is approximately 10^{-4} as compared with an efficiency of 10^{-3} for a comparable diode made by diffusion. The factor of 10 difference is due to the higher resistances which are obtained in the transmutation diodes. The area of the P-N junction writing surface of the transmutation diode is 16 square mils = 10^{-4} cm^2. Consider first a 100 milliampere current at 10 volts for 1 second. This consumes 1 joule of energy and produces 10^{-4} joule = 0.1 millijoule of infrared, leading to an energy density of

$$\frac{0.1 \text{ millijoule}}{10^{-4} \text{ cm}^2} = 10^3 \text{ millijoule/cm}^2$$

which is 50 times the minimum energy density. Thus a 20 millisecond pulse (1/50 of a second) would produce the required bleaching effect. Now if the pulsed current were not

100 ma for 20 milliseconds but
5 amperes for 0.4 milliseconds

the energy density would be the same. Thus one could bleach
with a pulse narrower than a millisecond.

Capacitive discharge circuits were tested for writing on
infrared film in very short time periods. In Section 7 we
show IR films in which writing was carried out in a fraction
of a millisecond.

5.2   Irradiation Techniques and Experimental Methods

The irradiation techniques which are used in the transmutation doping process are the following:

1) Fabrication of the radiation die

2) Insertion of semiconductor specimens into the radiation die in package form

3) Insertion of the radiation die packages into a radiation capsule

4) Insertion of the radiation capsule into the irradiation facility of the nuclear reactor

5) Specification of the irradiation time and monitoring of the neutron flux

6) Disassembly of the radiation capsule

7) Processing of the transmutation-doped semiconductor crystals. This includes
   Annealing
   Measurement of concentration changes
   Evaporation of ohmic contacts
   Electrical lead attachment
   Packaging of the diode array

These techniques will now be described in detail.

Fabrication of the Radiation Die

A ten mil thick cadmium layer was used to shield out thermal neutrons from the semiconductor, since this layer thickness gives almost complete opacity. It was decided to use mechanical fabrication techniques rather than photoresist methods for the first capsule, since no extremely narrow slit widths were required. Two configurations were selected for the first capsule:

1. The half-and-half configuration, in which half the
   semiconductor is shielded and half is unshielded.
   This configuration yields a single P-N junction at
   the boundary of the cadmium.

2. The multiple-diode array, in which alternate stripes
   of cadmium and stainless steel are attached to a metal
   base of steel or copper. This configuration yields a
   P-N junction at each interface between cadmium and
   non-cadmium.

These configurations were first made by spot-welding steel
spacers (10 mils thick) to a steel base with appropriate
spacing. Cadmium foil 10 mils thick was then cut to the
appropriate dimensions and were forced into place between
the steel spacers. Two steel spacers were also welded across
the pattern to serve as reference surfaces. Two identical
steel plates with the cadmium and steel pattern attached to it
constitute a radiation die. The dimensions of each plate are
approximately 1 inch by 1 inch by 50 mils. Holes are drilled
in these radiation dies for subsequent attachment together.

Another technique was also used to make the radiation dies.
A pattern of successive linear grooves was first pressed into a
lead plate. The grooves were then filled with cadmium stripes
cut to size. Two key grooves were also pressed into the lead
plate to hold steel key bars which would serve as reference
surfaces against which the semiconductor specimen would fit.

Both these techniques were adequate. However, the second
technique (pressing of a pattern into lead) is considerably more
economical in fabrication time.

It should be noted that steel, lead, and copper are all substantially transparent to neutrons in thicknesses of 10 to 100 mils. Only cadmium is opaque, and hence the pattern of cadmium and steel is effectively a set of slit in an otherwise opaque radiation die.

Insertion of Semiconductor into Radiation Die Packages

The semiconductor specimens are cut to the desired size, either by wafering or by cleaving. A cleaved surface is more efficient for subsequent infrared emission. One or two specimens are then inserted between the radiation die halves. The radiation die halves are held tightly together by wires and metal clip springs. The assembly is wrapped in aluminum foil and is called a radiation die package.

Radiation Capsule

The radiation capsule consists of a metal box or of metal plates between which the radiation die packages are placed. The function of the radiation capsule is simply to facilitate handling and to provide mechanical protection. Two to four packages may be placed in a capsule. Although the irradiation takes place under water, neither the packages nor the capsule is made water-tight, since the water is necessary for cooling purposes. A hook is attached to the radiation capsule for handling purposes.

Irradiation Procedure

The radiation capsule is placed at a pre-planned position on a shelf of the BSF irradiation facility. This facility consists of a large water tank just outside the core of a nuclear reactor.

Although the neutron flux in the irradiation location has been
previously mapped, it is expedient to monitor the flux during
irradiation by inserting cobalt monitor wires beforehand, which
can be removed during the course of the irradiation. The activa-
tion in the wires can be counted to give a measurement of the
neutron flux. At least one such flux reading is made during
each irradiation. Although the fluxes are expected to be of the
order of 0.9 to 1.4 x 10^{13} n cm^{-2} sec^{-1}, the perturbation
produced by the radiation capsule (and by other nearby objects
being irradiated) can significantly reduce the flux by 10% to 50%.
This leads to a requirement for a longer irradiation time.

Specification of Irradiation Time

When the neutron flux has been measured, one can select the
irradiation time required to insert the desired change in N type
impurity concentration. Let σ_T be the nuclear cross section
for transmutation - a macroscopic quantity measured in cm^{-1} which
includes both thermal neutron transmutations and non-thermal
transmutations. Then one has the relation

$$\varnothing * \sigma_T * t = \Delta N$$

where $\varnothing$ is the neutron flux, t is the irradiation time, and
ΔN is the desired change of dopant concentration in the semicon-
ductor. Since ΔN, σ_T and $\varnothing$ are known, this equation
permits specification of the irradiation time.

Instead of relying solely on flux monitor wires to measure
the flux we have used gallium arsenide specimens themselves as
monitors. These semiconductor monitors must be attached to the
capsule in such a way that they can be easily removed. They are
then read by measuring the change in concentration ΔN produced

by irradiation for a specific time. This concentration change is determined by measuring the Hall coefficient of the material (see below). This method has the advantage that it includes the effects of non-thermal as well as thermal transmutations. It was therefore used extensively in this work for both shielded specimens (completely surrounded by cadmium) and unshielded specimens.

Disassembly of the Radiation Capsule

Disassembly of the radiation capsule is done in a hot cell because of the radioactivity of the capsule components. Detailed instructions on this disassembly must be prepared for the hot cell operator. The semiconductor specimens have minimal radioactivity. Gallium arsenide specimens can be sent by common carrier one week after removal from the irradiation facility. The other capsule components have longer-lived radioactivity and must be disposed of at the reactor site.

Processing of the Transmutation-Doped Semiconductor Specimens

When the semiconductor specimens are received after irradiation they are first checked for radioactivity, then chemically cleaned. An annealing process is then carried out to remove radiation damage. The annealing process is done as follows: The gallium arsenide is placed in a quartz ampoule with excess arsenic to prevent evaporation of arsenic from the semiconductor. The ampoule is evacuated and flushed out with nitrogen. This process is repeated several times to flush out all the oxygen. The ampoule is then sealed off and heated for about 1/2 hour at 700 to $800^{\circ}C$. This removes the radiation-produced defects.

Concentration changes in each doped region are measured as
follows: One first cuts the individual regions of the semicon-
ductor apart using a diamond saw. It is necessary to have fairly
precise referencing of the individual regions in order to specify
how each semiconductor specimen is to be cut. Small ohmic
contacts are then placed on the periphery of the cut regions.
The technique for making ohmic contacts on both P and N type
specimens is described below. The Hall coefficient of the material
is next measured by attaching electrical leads to the ohmic
contacts and setting the specimen in a known magnetic field. The
Van der Pauw technique is used to measure the Hall coefficient.
From the Hall coefficient the net electronic concentration can be
calculated directly. The difference between the post-irradiation
concentration and the pre-irradiation concentration gives the
transmutation-induced concentration, ΔN.

Ohmic contacts are attached by vacuum evaporation onto the
specimen through a mask. The mask is a thin steel foil, about
1 mil thick, in which a pattern of holes corresponding to the
specimen region geometry has been photoetched. For N type
gallium arsenide, the evaporated metal is an alloy of indium and
tin in 80-20 ratio. For P-type gallium arsenide an 80-20 alloy
of indium and zinc has been used. These alloys generally give
ohmic contact.

Electrical leads are attached to these contacts by thermo-
compression ball bonding. The semiconductor specimen is mounted
on a flatpack microelectronic package and the gold wire leads from
the ball bonder are attached to the flatpack terminals.

The diode array is encapsulated in epoxy with only the
radiation-emitting end exposed. The epoxy is loaded with beryllia
(beryllium oxide) with high thermal conductivity for good heat
dissipation. This assembly is attached to a metal heat sink.

SECTION 6

Irradiation Experiments

It had originally been planned to perform the irradiations
for production of the diode array writing heads in the Oak Ridge
Reactor, with which we have extensive experience. Two capsules
were planned, one capsule to produce individual diodes and some
small arrays (five junctions or less) and one capsule to produce
larger arrays. However, after the photochromic material studies
were completed we were informed that increased usage of the
Oak Ridge Reactor by Oak Ridge National Laboratory would make
scheduling of experiments extremely uncertain. It was therefore
decided to use another available reactor, the Air Force Nuclear
Test Facility (AFNTF) at Wright Patterson Air Force Base.

The AFNTF is a "swimming pool" type of reactor, very similar
in design to the Oak Ridge Reactor, except that it operates at
a lower power. It was planned to perform the irradiations in the
BSF facility outside the reactor core. This is a large water tank
which is placed adjacent to the reactor vessel. Neutrons, both
thermal and fast, stream into the BSF from the reactor proper.
The specimens to be irradiated were contained within an aluminum
or steel capsule (the irradiation capsule) and placed on a shelf
at the inner edge of the BSF. The structure of the BSF is very
similar to the analogous water tank in the Oak Ridge Reactor.
It was thought that a preliminary monitoring of the neutron flux
level would provide the data necessary to determine the necessary
irradiation time. A flux monitor capsule was prepared. It
disclosed that the neutron flux was approximately 1×10^{13}
$n \ cm^{-2} \ sec^{-1}$, about half the value in the Oak Ridge Reactor.
This indicated that the irradiations could be identical to those
in the Oak Ridge Reactor, with the exception that the irradiations
would be about twice as long, i.e. about 200 hours as compared
with 100 hours in the Oak Ridge Reactor.

The first capsule was prepared and irradiated. It was found however that the gallium arsenide specimens had all been over-irradiated. Not only had the originally P-type unshielded regions been converted to N-type, but the shielded P-type regions, which should have remained P-type were also converted to N-type.

Detailed analysis of the first capsule specimens showed the reason for this over-irradiation. The cadmium ratio of the neutron flux spectrum in the AFNTF is 9 to 1, as compared with 39 to 1 in the ORR. What this means is that the non-thermal (higher energy) part of the neutron flux spectrum is significantly higher in the AFNTF than in the ORR. This is particularly important for gallium arsenide which has neutron absorption resonances at the higher neutron energies which are present in the AFNTF. The significance of the lower cadmium ratio in the AFNTF is presented in detail in Section 6.1.

Once this point was realized, a flux monitor capsule was prepared to measure this effect quantitatively. Results are given in Table 4 for a 100 hour capsule and in Table 5 for a 15 hour capsule. The significant results are the transmutation-induced concentration ΔN. The results indicate that for each 100 hours of irradiation, a ΔN of

(a) 3×10^{17} cm^{-3} is produced in gallium arsenide completely shielded by cadmium

(b) 7.5×10^{17} cm^{-3} is produced in gallium arsenide which is completely unshielded

The ratio of unshielded to shielded concentrations is 2.5 to 1, as compared with values of 6 to 1 which were obtained in the Oak Ridge Reactor. This means that for each 4.5×10^{17} cm^{-3} dopant atoms produced by thermal neutrons, there is an additional 3×10^{17} cm^{-3} produced by the epithermal neutrons absorbed by the gallium and arsenic resonances. The excess epithermal neutrons

are present because of the higher energy spectrum in the AFNTF.

The first irradiation capsule contained gallium arsenide with initial P-type concentration of 5.6×10^{17} cm^{-3} exposed for 200 hours. It was expected that the unshielded regions (slits in the radiation die) would experience a ΔN of

$$\Delta N = 2 \times 4.5 \times 10^{17} \text{ cm}^{-3} = 9 \times 10^{17} \text{ cm}^{-3}$$

Thus the original 5.6×10^{17} P-type concentration would convert to $(9-5.6) \times 10^{17} = 3.4 \times 10^{17}$ N-type. The shielded regions were expected to experience a ΔN of $1/6 \times 9 \times 10^{17} = 1.5 \times 10^{17}$ to give a final P-type concentration of

$$(5.6-1.5) \times 10^{17} = 4.1 \times 10^{17} \text{ cm}^{-3}$$

However, the large epithermal spectrum gives a ΔN of 3×10^{17} cm^{-3} for each 100 hours even in the shielded region. Hence even these regions are converted to N-type by an amount

$$(5.6-6) \times 10^{17} = 0.4 \times 10^{17} \text{ cm}^{-3} \text{ P type}$$

It is for this reason that Capsule 1 was over-irradiated.

Once this point was clarified, one could select an irradiation time to make the desired diode configurations in Capsule 1. Capsule 1 was redone with an appropriate selection of the irradiation time. This is described in Section 6.2. The diodes were properly doped, including a 4-diode array which was made into an infrared writing head. This writing head is described in detail in Section 7.

The selection of the irradiation conditions for the successful capsule is described in Section 6.2. In Section 6.1 the effect of the cadmium ratio (high epithermal spectrum) of the AFNTF on gallium arsenide transmutation doping is discussed.

6.1 Effect of the Neutron Flux Spectrum (Cadmium Ratio) on Transmutation Doping in Gallium Arsenide

The following expression can be given for the N-type transmutation concentration from either gallium or arsenic in gallium arsenide:

$$\Delta N = \sigma_T \phi t \left[\frac{0.82}{G_T} + 1.6 \alpha + \alpha \frac{I_r}{\sigma_T} \right] \quad (1)$$

where σ_T = macroscopic thermal transmutation cross section in cm^{-1}

       ϕt = product of neutron flux times time

       α = ratio of epithermal neutron flux to thermal neutron flux

       G_T = thermal flux depression factor of the irradiation capsule

       I_r = resonance absorption integral (in the neutron energy range of 0.3 to 1 ev) of gallium or arsenic

The cross section values are as follows:

$$\sigma_T (gallium) = 0.054 \ cm^{-1}$$

$$\frac{I_r}{\sigma_T} (gallium) = 4.7$$

$$\sigma_T (arsenic) = 0.096 \ cm^{-1}$$

$$\frac{I_r}{\sigma_T} (arsenic) = 7.5$$

The α value is related to the cadmium ratio (designated CdR) of the reactor flux spectrum by the following approximate expression:

$$\alpha = \frac{0.82}{2(CdR - 2)} \qquad :)$$

In the Oak Ridge Reactor irradiation facility the cadmium ratio is 39. This gives an α value of

$$\alpha \approx 1.2 \times 10^{-2}$$

Thus the relative values of the three terms in equation (1) for arsenic are (assuming $1/\sigma_T = 0.7$)

$$\Delta N = \sigma_T \emptyset t \left[0.57 + .019 + 0.09 \right]$$

Therefore the thermal transmutations predominate in the Oak Ridge Reactor.

In the AFWTF irradiation location however, the cadmium ratio was determined to be only 9. This gives an α value of

$$\alpha = 5.85 \times 10^{-2}$$

The relative values of the terms in equation (1) for arsenic are now

$$\Delta N = \sigma_T \emptyset t \left[0.57 + 0.10 + 0.44 \right]$$

Table 4
Data on 100-Hour Irradiation
Flux Monitor Capsule

Flux reading within radiation die = 0.59×10^{13} n cm^{-2} sec^{-1}
(from cobalt monitor foil)

Unshielded gallium arsenide $\Delta N = 7.4 \times 10^{17}$ cm^{-3}

Completely shielded gallium arsenide $\Delta N = 3.0 \times 10^{17}$ cm^{-3}

Table 5
Data on 15-Hour Test Irradiation
in Flux Monitor Capsule

Specimen	Type	Initial Concentration ($\times 10^{17}$ cm^{-3})	Final Concentration ($\times 10^{17}$ cm^{-3})	N ($\times 10^{17}$ cm^{-3})
C	Unshielded	3.5 (P)	2 (P)	1.5
D	Shielded	3 (P)	2.5 (P)	0.5
G	Unshielded	3.5 (P)	2 (P)	1.5
A	Unshielded	0.7 (N)	2 (N)	1.3

Table 6
Data on 60-Mil Junction Arrays
Capsule 2 Irradiation

	Specimen 1	Specimen 2
Initial Concentration	4.8×10^{17} (P)	5.6×10^{17} (P)
Final Concentration under 60-mil unshielded slits	4.0×10^{17} (N)	2.5×10^{17} (N)
$\triangle N$, Unshielded Slits (transmutation-induced concentration)	8.8×10^{17}	8.1×10^{17}
Final Concentration shielded regions	1.4×10^{17} (P)	1.4×10^{17} (P)
$\triangle N$, Shielded Regions (transmutation-induced concentration)	3.4×10^{17}	4.2×10^{17}

Thus the non-thermal transmutations constitute about half of the total in arsenic. In gallium the ratio is about one third. When one adds the transmutation effects in gallium and arsenic together one finds that about 40% of the transmutations are due to non-thermal neutrons. These calculations explain the data given in Table 4 where it is shown that completely shielded specimens (which display only the non-thermal transmutations) obtain 40% of the ΔN that is found for the completely exposed specimens.

The data of Table 4 may be analyzed as follows:

Let x = the ratio of transmutations above the
cadmium cutoff neutron energy (about 0.3 ev)
to the thermal transmutations

Then the ratio of transmutations in a completely unshielded gallium arsenide specimen to one completely shielded by cadmium is given by

$$\frac{\text{unshielded transmutations}}{\text{shielded transmutations}} = \frac{1 + x}{x}$$

From Table 4 one finds this ratio to be 7.4/3. Solving for x one obtains

$$x = 2/3$$

Table 4 also gives the thermal flux measured in a radiation die which takes into account the flux depression by the cadmium pattern with a slit in it. This is an important quantity in predicting the required irradiation. We wish to derive a flux depression factor from it. This can be done as follows:

First one asks what is the unperturbed thermal flux $\emptyset$. (We already have the perturbed flux 5.9×10^{12} n cm^{-2} sec^{-1} from Table 4 . The ratio of the two is the flux depression factor.) $\emptyset$ satisfies the following equation.

$$\sigma_T \, \emptyset t \, (1 + x) = 7.4 \times 10^{17} \, cm^3$$

The right hand side is the transmutation-induced concentration
in the unshielded specimen of Table 4 . σ_T is the thermal
transmutation macroscopic nuclear cross section, $0.15 \, cm^{-1}$ for
gallium arsenide, and t is the time = 100 hours = 3.6×10^5
seconds. Inserting these values and solving for $\emptyset$ one obtains

$$\emptyset = 8.5 \times 10^{12} \, n \, cm^{-2} \, sec^{-1}$$

The thermal flux depression factor is therefore

$$\frac{5.9 \times 10^{12}}{8.5 \times 10^{12}} = 0.7$$

Actually this value is inexact because the flux value measured
by the cobalt wire $(5.9 \times 10^{12} \, n \, cm^{-2} \, sec^{-1})$ includes non-thermal
absorptions. Since the cadmium ratio of cobalt foil is 9 to 1,
11% of the 5.9×10^{12} is non-thermal and the thermal flux is
$5.3 \times 10^{12} \, n \, cm^{-2} \, sec^{-1}$. Thus the corrected thermal flux
depression factor is

$$\frac{5.3 \times 10^{12}}{8.5 \times 10^{12}} = 0.63$$

Note how much more effective the non-thermal flux is in
causing transmutations than the thermal flux. In this location
the unperturbed thermal neutron flux is

$$8.5 \times 10^{12} \, n \, cm^{-2} \, sec^{-1}$$

while the non-thermal neutron flux is only about 1/10 this value:

$$\text{epithermal flux} = 0.85 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$$

This we know from the cadmium ratio (9 to 1) of the flux.

Nevertheless, the thermal flux produces only about 50% more transmutations than the epithermal flux according to Table 4 .

$$\text{Thermal flux produces} \quad (7.4-3) \times 10^{17} \text{ cm}^{-3}$$
$$= 4.4 \times 10^{17} \text{ cm}^{-3}$$

$$\text{Epithermal flux produces} \quad 3 \times 10^{17} \text{ cm}^{-3}$$

This is because of the large absorption resonances of gallium and arsenic and because of the low cadmium ratio (relatively high epithermal flux) of the irradiation location.

It is interesting to test the consistency of the data of Table 4 with the 9 to 1 value measured for the cadmium ratio. The ratio $1+x/x$ can be expressed in terms of equation (1) of this section:

$$\frac{1 + x}{x} = \frac{0.82 + 1.6\alpha + 6.5\alpha}{1.6\alpha + 6.5\alpha}$$

where 6.5 is an average resonance integral value for gallium and arsenic. Inserting the value $x = 2/3$ obtained above, one finds:

$$\frac{5}{2} = \frac{0.82 + 8.1\alpha}{8.1\alpha} = 1 + \frac{0.10}{\alpha}$$

giving a value $\alpha = 0.067$. This compares with the previously cited value of 0.0585, obtained from the measured cadmium ratio.

Table 5 gives an alternate set of data taken in a 15-hour irradiation. This data indicates the ratio of transmutation-induced concentrations (unshielded to shielded) may be as high as 3 to 1, as compared to the 2.5 to 1 ratio of Table 4. This would correspond to an α value of 0.050. The mean of these two values 0.050 and 0.067 compares favorably with the cited value of 0.0585 obtained from the cadmium ratio. The difference in values between Tables 4 and 5 can be attributed to variations in the flux and to uncertainties in the concentration readings.

6.2 Selection of Irradiation Conditions

The basic data for selection of the irradiation conditions in the successful capsule can be restated from the analysis of Section 6.1. This data is the following:

1. For each 100 hours of irradiation in the location used, a gallium arsenide specimen completely <u>shielded</u> by cadmium experiences a transmutation-induced concentration change of 3×10^{17} cm^{-3} N-type.

2. For each 100 hours of irradiation in the location used, a gallium arsenide specimen completely <u>unshielded</u> by cadmium experiences a transmutation-induced concentration change of 7.4×10^{17} cm^{-3} to 9×10^{17} cm^{-3} N-type.

3. Within a 60-mil wide slit in a (10-mil thick) cadmium radiation die, the thermal neutron flux is 0.63 of its value for a completely unshielded specimen. For different slit widths one can calculate similar values on the basis of the radiation die geometry. If one denotes this inverse flux depression factor by 1/G one obtains the values of .55 for a 45 mil spacing and .50 for a 30 mil spacing.

Using these   three data items, one can calculate the ratio of transmutations induced in the slit to transmutations induced under the cadmium. In one hundred hours   the transmutations induced under the slit in the radiation die are

$$3 \times 10^{17} + \frac{1}{G} (7.4-3) \times 10^{17}$$

where $1/G = 0.63$ for 60 mil slits in the radiation die, for which experimental data is given in Table 6 . The calculated ratio of transmutations under the slit to those under the cadmium is

$$\frac{3 \times 10^{17} + 0.63 \times 4.5 \times 10^{17}}{3 \times 10^{17}} = 2$$

We have used the lower limit, 7.4×10^{17} cm^{-3} figure for transmutations induced in the unshielded specimen. If we had used the upper figure, one would obtain 2.25.

The ratios implied in Table 6 are in good agreement with these figures for 60-mil slits in radiation dies. For the initial concentration of 4.8×10^{17} one obtains a ratio of 2.6. For the initial concentration of 5.6×10^{17} one obtains a ratio of 1.93.

The irradiation described by Table 6 took 120 hours. This selection of the irradiation time was made to satisfy the criteria that

1) In the shielded regions the gallium arsenide must remain P-type

2) In the regions under the slits the gallium arsenide must convert to N-type

Since the material was initially P-type, the first condition sets an upper limit on the irradiation time. For example, in the 4.8×10^{17} cm^{-3} P-type material, 120 hours would be expected to add

$$\frac{120}{100} \times 3 \times 10^{17} \text{ cm}^{-3} = 3.6 \times 10^{17} \text{ cm}^{-3}$$

N-type impurities, to bring its final concentration to

$$(4.8-3.6) \times 10^{17} \text{ cm}^{-3} = 1.2 \times 10^{17} \text{ cm}^{-3} \text{ P type}$$

The actual final concentration in this region was 1.4×10^{17} cm^{-3}. Note that another 50 hours of irradiation would have converted these regions to N-type, thus eliminating the P-N junctions.

In the regions under the slit the transmutation-induced concentration is expected to be 2 to 2.25 times greater than in the shielded region. Using the 2.25 figure one would expect a ΔN of

$$\Delta N = 2.25 \times \frac{120 \text{ hours}}{100 \text{ hours}} \times 3 \times 10^{17} \text{ cm}^{-3}$$

$$= 8.1 \times 10^{17} \text{ cm}^{-3}$$

The actual ΔN was somewhat higher as shown in Table 6 .

Since this concentration is N-type, the original P-type concentration of 4.8×10^{17} is converted to N-type. The final N-type concentration is expected to be

$$(8.1-4.8) \times 10^{17} \text{ cm}^{-3} = 3.3 \times 10^{17} \text{ cm}^{-3} \text{ N-type}$$

The actual value was measured to be $4 \times 10^{17} \text{ cm}^{-3}$ N-type.

A longer irradiation time would increase this value, but if the irradiation time were sufficiently shorter, i.e. less than 70 hours, the region under the slit would not convert to N-type and no P-N junctions would be formed. These are the types of considerations involved in selection of the irradiation time, as dependent on the initial concentration of the material and the transmutation characteristics in the reactor.

SECTION 7

Fabrication of a Four-Channel Diode Array Film Recorder

The successful gallium arsenide irradiation capsule included several specimens which had been exposed with radiation dies to produce four-element arrays. One of these four-junction diode arrays was fabricated into a four-channel film writing head, which was tested successfully on 35 mm infrared film. A simple four-channel film recorder was built and demonstrated. The recorder was delivered to the U.S. Navy Underwater Sound Laboratory, New London, Connecticut. This four-channel diode array film recorder will now be described as typical of larger arrays which can be built.

The junction spacing in the diode was nominally designed to be 60 mils. Irregularities in the radiation dies led to some irregularities in the spacings. Three of the junctions were more efficient than the fourth. This is apparent in Figure 7 which shows film exposures.

Fabrication of the diodes from the doped array is performed as follows: The P-type regions were masked and a dot pattern of silver-indium-tin alloy was evaporated onto the N-type regions. The N regions were then masked and a dot pattern of silver-indium-zinc alloy was evaporated onto the P-type region. After baking the evaporated contacts at $575^{\circ}C$ for about 10 minutes, the doped wafer was cleaved into 50-mil wide regions. A thermocompression bonder (Kulicke & Soffa, Inc.) was used to connect the evaporated dots electrically into a standard microelectronic flatpack. This bonding is done at $500^{\circ}C$ under forming gas. If forming gas is not used in sufficient quantity, an oxide builds up on the gallium arsenide. This oxide layer provides a leakage path across the junction in forward bias, as well as in reverse bias, and therefore lowers the high reverse voltage capability. Care should be taken to prevent formation of this oxide layer.
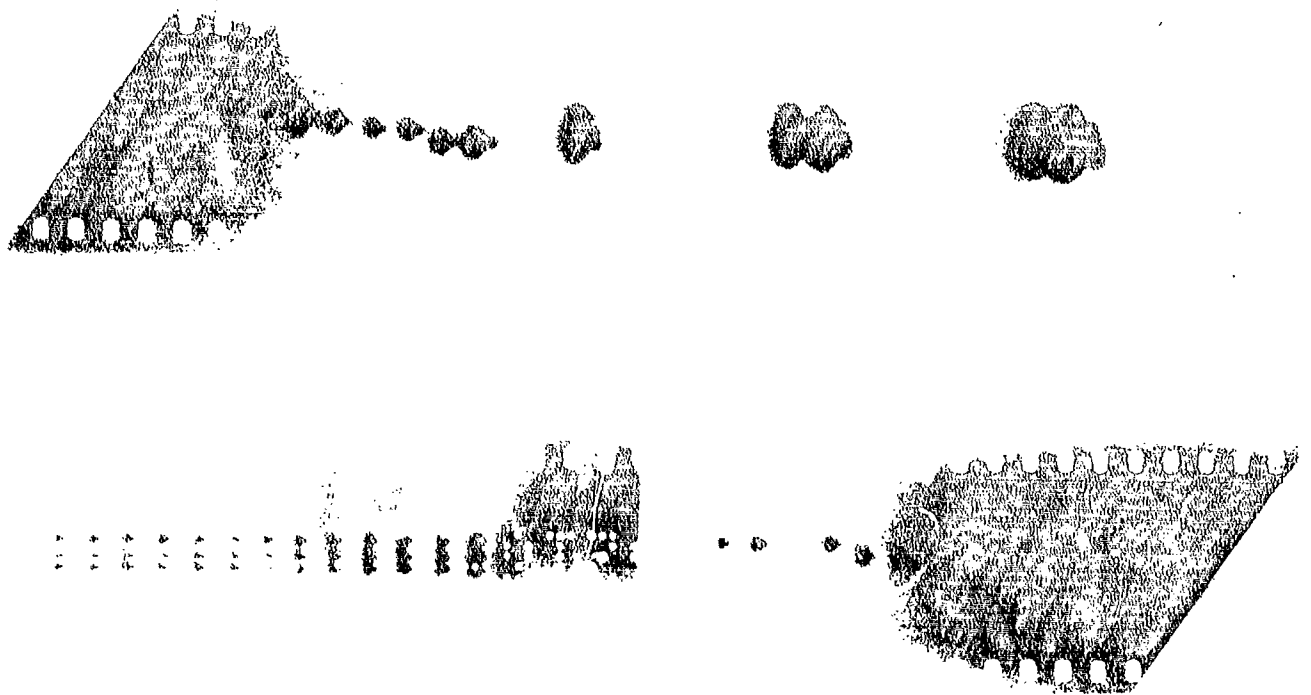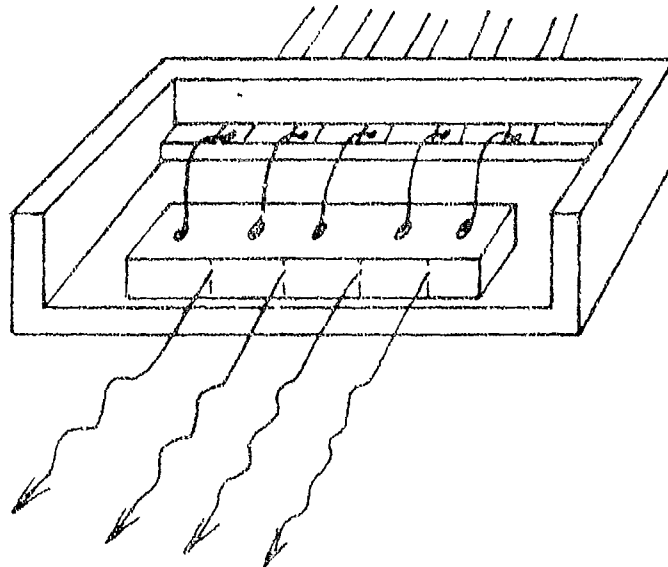
Figure 7.   Film Exposures from Four-Diode Array

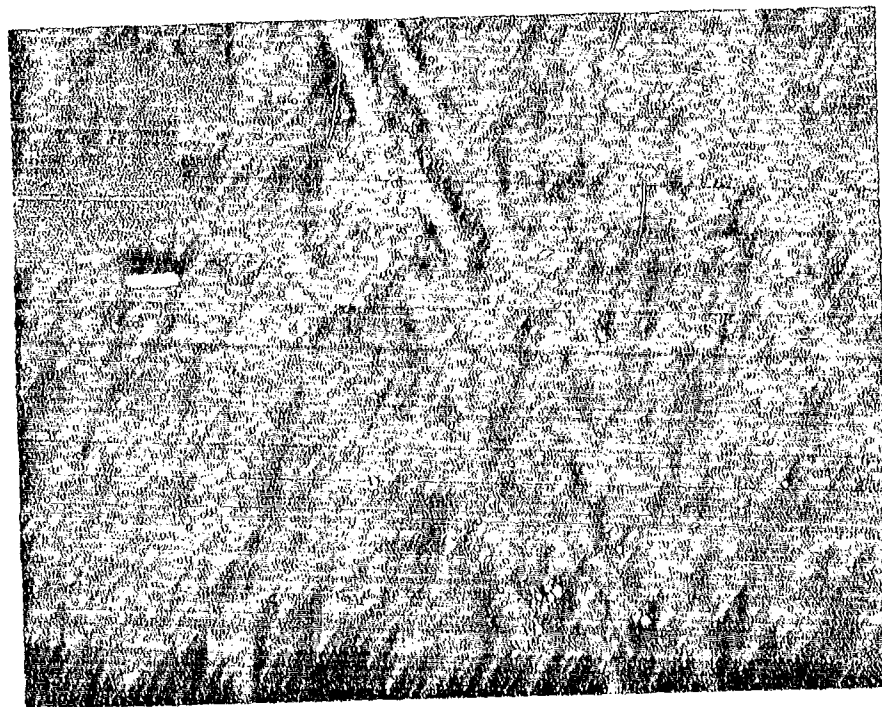Figure 8. Mounted Diode Array

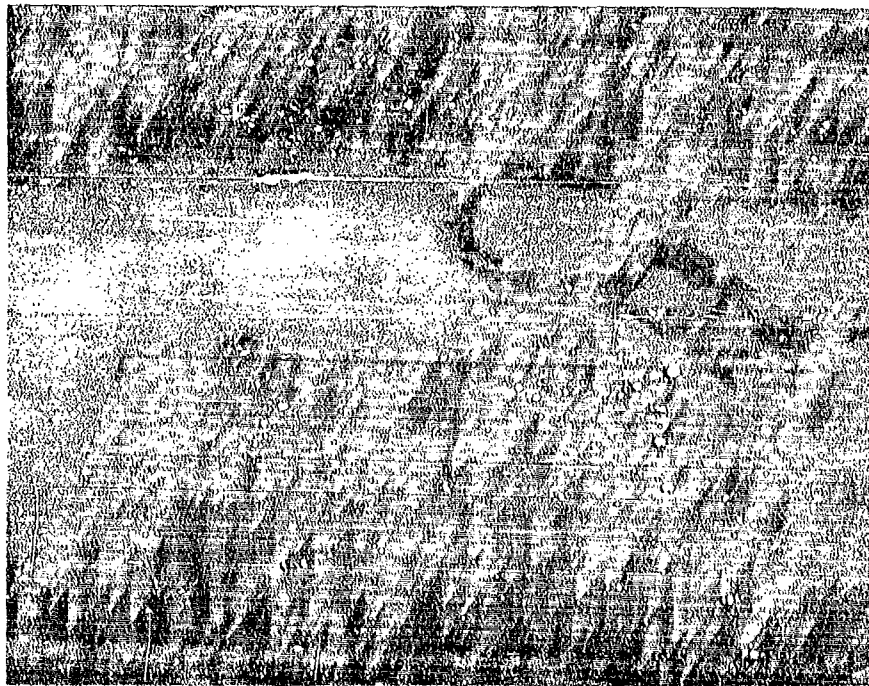Figure 9.   Diode Array Mounted on Socket
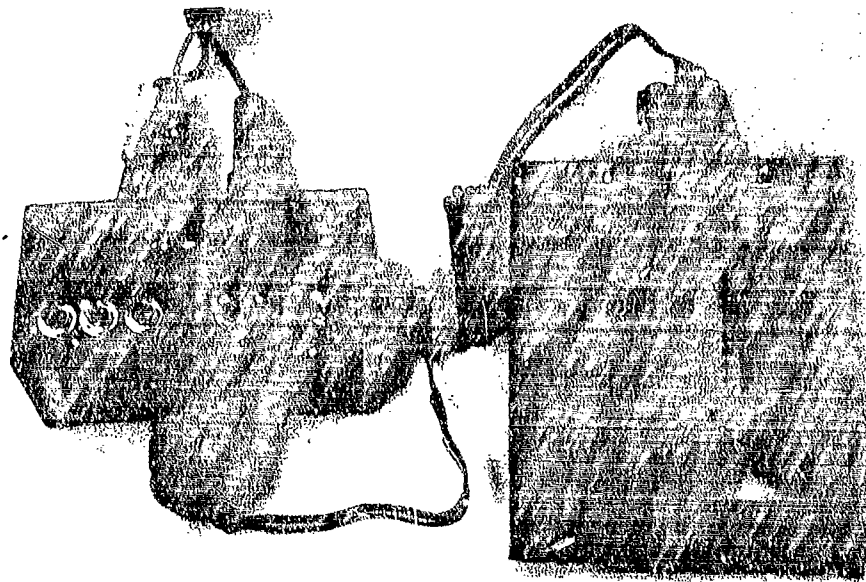
Figure 10. Side View of Writing Head

Figure 11. Writing Head with Control Box

In order to demonstrate the use of the array as a writing head, a mounting apparatus has been built. The diode array is mounted on a 3/8" by 3/8" seven-lead standard microelectronic flatpack, which was cut in half to permit one surface to be flush with the diode array and the film. The array lies flat on the base of the flatpack, thus setting the exposed writing surface of the junctions at $90°$ to the base of the pack. A diagram of the flatpack mounting arrangement is shown in Figure 8. The infrared radiation is therefore emitted through the cut end of the pack as shown.

The writing head is mounted to place the large area face of the diode array wafer at right angles to the film. The exposed writing surfaces of the junctions are thus parallel to the film and in direct contact with the film. The dimensions of the dot recorded on the film are about 10 mils by 4 mils and the four dots are nominally 60 mils apart.

This mounting arrangement was achieved by placing the flatpack containing the array in a flatpack socket mounted as follows: The flatpack socket was cut in half and fastened to a 2" by 2" by 1" plexiglass block. Adjustment screws were provided to make small modifications in the orientation of the diode array. The plexiglass block was mounted on a base which permits it to pivot on the side of the block opposite the flatpack. Springs were inserted on the pivots to permit the block to be raised when the film is advanced. The springs permit the pressure of the diode array on the film to be adjusted. Tracks are fastened to the plexiglass mounting base to guide the motion of a 35 mm film strip.

Figure 9 is a photograph showing the diode array (dark) mounted on the flatpack (light, with wires) set into the flatpack socket normal to the film. Figure 10 is a side view photograph of the writing head with the diode array detached and placed in the

foreground. Figure 11   is a photograph of the writing head
apparatus with its control box. Figure   7   shows some recorded
dot patterns on film. These have been intentionally overexposed
to make them more visible.

The control box for the array is used for addressing the
individual junctions of the array. It consists of a box with
six single pole switches. These are alternately connected to
the two output poles on a double pole double throw switch. Thus
one can choose the output from the addressing unit to be +-+-+-
or -+-+-+. The outputs go to the alternate P and N type regions
of the diodes. Thus the individual junctions may be either
forward-biased, reverse-biased, or not biased at all.

The diode array was embedded in a heat dissipating beryllium
oxide resin after the photographs shown above were taken. Exposures
were first made at 50 milliamperes (about 10 volts) for one second.
The power supply should be current-limited (constant current supply)
to prevent high current surges which might destroy the array.

The writing speed of this device with infrared film is
very fast. It should be noted that conventional silver halide
films operate with energy densities at least 10^5 times faster
than photochromic films, and we have seen that luminescent diodes
should be able to write on photochromic films at millisecond rates.

The theoretical writing speed of this array is limited by
the RC time constant of the diode or by the carrier lifetime,
whichever is the longer. Carrier lifetimes at the 10^{17} cm^{-3}
concentration level in gallium arsenide are in the nanosecond
range. The RC time constant of a diode will also be in the
nanosecond range since $R \sim 50$ ohms and $C \sim 10$ pf have been
measured. Hence writing speeds should be in the gigacycle range.
Since the writing head will depend on mechanical transport of the
film, it seems apparent that the film transport speed will set
the ultimate limit, and not the characteristics of the device.

No careful tests were made to measure the maximum writing speed. However, dot sets have been recorded in less than a millisecond by discharging a capacitance through the diodes. In these tests the optical pulse length was set by the magnitude of the discharging capacitance and by the bulk resistance of the diodes.